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THE USE OF A MERCURY CATHODE IN ELECTROCHEMICAL ANALYSIS.

BY EDGAR F. SMITH.

Received June 26, 1903.

THE suggestion of precipitating metals in the form of amalgams was first made (1880) by Wolcott Gibbs,[1] who described a new scheme for the electrolytic determination of metals, before the National Academy of Sciences, in which scheme he recommended weighing out in a small beaker a definite amount of metallic mercury which was, by means of a platinum wire, connected with a battery and made the cathode, while in the salt solution, contained in the beaker, was suspended a strip of platinum, serving as the anode. The currents used varied greatly in strength. Salts of mercury, tin and cobalt were apparently decomposed, their respective metals being precipitated upon or in the mercury cathode. Quantitative results do not appear. The author of this method believed that possibly sodium and potassium might be separated in this manner and Professor Hunt remarked that the "process came with the beauty and force of a revelation."

[1] *Chem. News*, **42**, 291.

Three years later (1883) Wolcott Gibbs[1] again directed attention to "the employment of mercury as negative electrode, the positive electrode being a plate of platinum..... It was found possible to separate iron, cobalt, nickel, zinc, cadmium and copper so completely from solutions of the respective sulphates that no trace of metal could be detected in the liquid..... the author had in view both the determination of the metal by the increase in weight of the mercury, and in particular cases of the molecule combined with the metal, either by direct titration or by known gravimetric methods." The experiments were purely qualitative, such being, in the author's opinion, sufficient to establish the correctness of the principle involved.

In 1886 Luckow,[2] cognizant of the difficulties attending the determination of zinc in the electrolytic way, described a course for this purpose which consisted in weighing out in a platinum dish a quantity of metallic mercury or its oxide, introducing the zinc salt solution and then electrolyzing, when the zinc, combined with the mercury, spread over the inner surface of the dish as a beautiful, adherent amalgam.

Nothing further was done towards the development of the ideas outlined in the preceding paragraph until 1891, when Vortmann[3] described, at considerable length, the determination of several metals in the form of amalgams. His plan consisted in adding a weighed quantity of mercuric chloride to the solution of the salt to be electrolyzed, the metals being then precipitated together. The results were quite interesting and seemed to offer decided advantages, but later experience demonstrated that, except in a few cases, this method of analysis, as elaborated by Vortmann, was in nowise superior to the usual procedure in determining metals electrolytically.

A few months later, in the same year (1891), Drown and McKenna,[4] striving to find a method suitable for the estimation of small amounts of aluminum in the presence of a preponderance of iron, had recourse to the suggestion of Wolcott Gibbs. They accordingly weighed a beaker containing a layer of mercury (the cathode), and introduced into the solution of the metals a platinum plate (the anode). The current was allowed to act through the

[1] *Am. Chem. J.*, **13**, 571.
[2] *Chemiker-Zeitung*, **9**, 338 and *Ztschr. anal. Chem.*, **25**, 113.
[3] *Ber. d. chem. Ges.*, **24**, 2749.
[4] *J. anal. Chem.*, **5**, 627.

night and the iron was completely precipitated in the mercury. The aluminum remained in the slightly acidulated solution. These chemists encountered several difficulties in pursuing this course. The platinum wire projecting into the mercury often had iron precipitated upon it, so that it became necessary to weigh the wire, enclosed in a glass tube, together with the beaker of the mercury. Further, much annoyance was experienced in the efforts to dry the amalgam and obtain constant weights.

The preceding paragraphs comprise all that is to be found in the literature of electrochemical analysis, relating to amalgams and the use of mercury as a cathode in metal precipitations.

The thought of the writer had many times dwelt upon the facts mentioned above until at length it was determined to conduct a series of experiments with mercury as cathode, to establish two

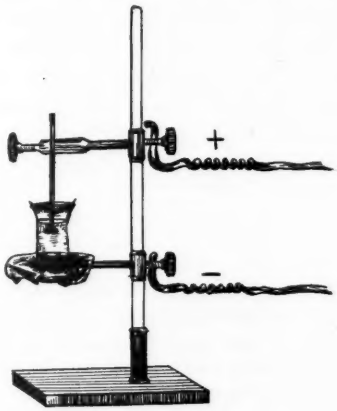

Fig. 1.

points: (*a*) The determination of the negative radical in various salts as well as the metals combined with them, and (*b*) the possibility of effecting the separation of certain metals.

To this end, practically the same device as that used by Drown and McKenna was adopted. Into the mercury, serving as cathode, there extended a glass tube from the lower end of which projected a carbon pencil, 1 mm. in length. This pencil of carbon was preferable to the platinum wire; metals did not adhere to it and, therefore, it was not necessary to weigh it together with the beaker and the mercury. The glass tube was nearly full of mer-

cury, into which dipped a copper wire connected with the negative binding-post. Such was the form of apparatus first used.

I. ELECTROLYSIS OF SULPHATES.

The sulphate first chosen was that of copper. A weighed amount of the salt was dissolved in water; the volume of its solution, when introduced into the apparatus mentioned above, equaled about 50 cc. It was electrolyzed at the normal temperature with the conditions given below. Sometimes during the electrolysis "copper trees" appeared on the surface of the mercury cathode (22 sq. cm. in area). They disappeared on gently shaking the beaker. This agitation was sufficient to make them amalgamate. When the liquid had become colorless, it was carefully siphoned into a beaker, its place being taken by distilled water. The washings accumulated in this manner equaled about 500 cc. The current was then interrupted. The sulphuric acid in the liquid conveyed away by the siphon was determined by titration with a tenth-normal sodium carbonate solution. The mercury cathode containing the copper was dried first with bibulous paper and then by standing for a number of hours over sulphuric acid, after which it was weighed.

Number.	Time. Hours.	Ampere. N.D$_{100}$.	Volts.	Cu present. Gram.	Cu found. Gram.	Cu present. Per cent.	Cu found. Per cent.	H_2SO_4 present. Gram.	H_2SO_4 found. Gram.	SO_4 present. Per cent.	SO_4 found. Per cent.
1	5	0.02–0.10	2.25–5.0	0.1512	0.1495	25.30	25.02	0.2352	0.2355	38.55	38.50
2	3½	0.08–0.12	4.25–5.5	0.1512	0.1499	25.30	25.08	0.2352	0.2347	38.55	38.47
3	4½	0.08–0.12	3.5–4.0	0.3024	0.3002	25.30	25.11	0.4704	0.4694	38.55	38.47
4	4½	0.10–0.13	4.0–4.5	0.3024	0.2986	25.30	25.00	0.4704	0.4723	38.55	38.80

The anode in Experiments 1, 2 and 3 was a strip of platinum foil, while in Experiment 4 it was a spiral of platinum.

It will be observed that, so far as the results are concerned, those relating to the metal fall below the theoretical requirement, while in the case of those bearing upon the acid they approximate theory more closely. Difficulty was experienced in drying the amalgam. Drown and McKenna had the same trouble. It seemed at first that it might prove detrimental to the general adoption of the method in ordinary analysis. It was, however, successfully overcome, for it was found that the amalgam could be washed with alcohol and ether, thus removing the final traces of water,

and that not more than fifteen minutes would then be necessary for the drying of the metal. A number of carefully conducted tests established this point. Mr. W. M. Howard of this laboratory also devised the following plan to eliminate the use of the anode of Drown and McKenna, as well as the carbon pencil.

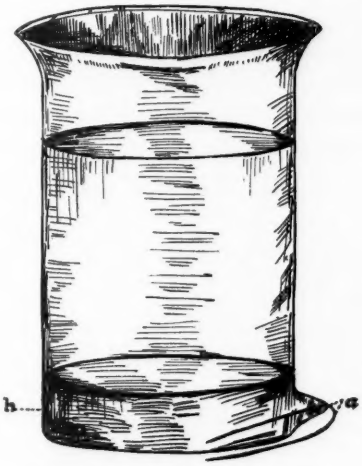

Fig. 2.

It is an extremely simple contrivance, consisting of a small beaker (50 cc. capacity), near the bottom of which there is introduced, through the side, a thin platinum wire. Internally it dips into the mercury, while externally it touches a disk of sheet-copper on which the beaker rests and which is connected with the negative electrode of a cell, thus making the mercury the cathode. By adopting this device and by washing the amalgam with alcohol and ether, the two chief disturbing factors were removed. Thus, on subsequently electrolyzing a copper sulphate solution containing 22.61 per cent. Cu and 41.20 per cent. SO_4, there was obtained

(*a*) 21.61 per cent. Cu..... 41.23 per cent. SO_4.
(*b*) 21.70 " " " ..... 41.23 " " "

and on substituting a nickel sulphate solution, using a current of 0.05 to 0.06 ampere and 4 volts, the results were

30.41 per cent. Ni ..... 50.75 per cent. SO_4.
30.40 " " " ..... 50.76 " " "

while the theoretical requirements were

30.40 per cent. Ni .... 50.70 per cent. SO_4.

With zinc sulphate, a current of 0.26 ampere and 6 volts acted for six hours, giving

(*a*) 24.27 per cent. Zn ..... 36.71 per cent. SO_4.
(*b*) 24.37 " " " ..... 36.61 " " "

while the quantities present were

24.30 per cent. Zn ..... 36.60 per cent. SO_4.

In sphalerite, the zinc determined volumetrically equaled 65.7 per cent., while a second portion of the same mineral rapidly decomposed with nitric acid and evaporated with hydrochloric acid, furnished a solution, which on electrolyzing with a mercury cathode showed 65.6 per cent. Zn.

In ferrous ammonium sulphate, electrolyzed in the same fashion, the following percentages of iron were found: 14.26, 14.28, 14.33, 14.19, 14.25 per cent., the theoretical being 14.28 per cent.

Additional data might be given to show that with a mercury cathode it is possible to electrolyze sulphates like those mentioned above and thus determine both the metals and the molecules with which they were in combination. It is needless to add that from such metals phosphoric acid, also, might be easily separated and determined in this way.

For quite a while the writer had been striving to effect, in the electrolytic way, the separation of iron from uranium. On observing the readiness and completeness of the precipitation of iron in the mercury, steps were at once taken to try this method in the hope of effecting the above separation. One-tenth of a gram of each metal was present in the solution in the form of sulphate. To this was added 0.25 cc. of 50 per cent. sulphuric acid and the liquid then electrolyzed with a current of 0.25 to 0.5 ampere and 6 to 8 volts for four and one-half to five hours. The iron was precipitated free from uranium. The separation was repeated several times with like satisfactory results. It may also be added that quantitative separations of iron from titanium, from zirconium and from thorium were made and the results were most satisfactory. In these separations the pressure did not exceed 5

volts with a cathode surface of 22 sq. cm. The precipitation of the iron was finished in five hours, although several trials were conducted through the night. The ordinary temperature prevailed in the separations. The quantity of each metal present was 0.1 gram. The found percentages of iron from titanium were 14.15, 14.20 and 14.21 per cent.; of iron from zirconium, 14.28 and 14.42 per cent.; of iron from thorium 14.31, 14.38 and 14.32 per cent., instead of the required 14.28 per cent.

II. THE ELECTROLYSIS OF METALLIC NITRATES.

Having ascertained that sulphates could be completely analyzed as indicated in the preceding paragraphs, it was only natural to turn to nitrates. Previous experience had taught that in such cases the acid radical instead of being released as such was reduced to ammonia. But this, it was believed, could be readily estimated if, before commencing the electrolysis of the nitrate, a definite volume of sulphuric acid of known strength should be added. When the electrolysis was finished, the free residual sulphuric acid could be titrated and the difference between its quantity and that originally introduced would give a difference which was combined with the ammonia. It would be a mere matter of calculation to arrive at the quantity of nitric acid previously combined with the metal. Guided by this thought a trial was instituted. The theoretical amount of metal was deposited in the mercury cathode, but upon titrating the sulphuric acid a volume of tenth-normal sodium carbonate equivalent to it was not only consumed, but in addition a volume sufficient to neutralize the nitric acid in union with the metal. In other words, the nitric acid had not been reduced to ammonia. It will be recalled that Vortmann[1] described a method for the determination of nitric acid which consisted in reducing the acid to ammonia in the presence of copper sulphate and sulphuric acid. This knowledge led to several repetitions of the experiment with like results, *viz.*, complete precipitation of the metal and liberation of the nitric acid. Nickel nitrate was the salt more particularly studied, although other nitrates showed a like behavior:

Nickel present. Per cent.	Nickel found. Per cent.	NO_3 present. Per cent.	NO_3 found. Per cent.
20.27	20.06	42.61	42.24
....	20.07	....	42.02
....	20.28	....	41.70
....	20.28	....	....

[1] *Ber. d. chem. Ges.*, **23**, 2798.

These results were obtained with a current of 0.1 to 0.2 ampere and 3 to 3.5 volts. The time allowed was six hours. Search was made for ammonium salts but none were found, from all of which it would appear that the mercury cathode allowed of the complete determination of the acid and metal portions of nitrates, as well as of sulphates.

III. ELECTROLYSIS OF HALIDES.

Could the haloid acids be similarly determined? Several years ago Vortmann[1] published an account of the estimation of iodine in potassium iodide. Later Specketer[2] announced an electrolytic separation of the halogens. In neither instance was the estimation of the associated metal considered.

To begin, the writer set himself the problem of determining the sodium and the chlorine in ordinary salts. The small beaker, pictured on p. 887, was used. At first, silver-plated strips of platinum were made to serve as anodes. Very soon it was found that, as silver chloride was produced on these plates and loss took place in the drying of the same, anodes of platinum gauze coated with silver would answer better. It very shortly became evident that the chlorine was quantitatively deposited on these anodes. The method of procedure then became this: About 50 grams of pure mercury were put into the beaker, which was then weighed. The aqueous solution of a weighed amount of salt was introduced, the volume of liquid equaling about 40 cc. In this solution the weighed, silver-coated, platinum gauze was suspended. The current was then permitted to pass at the ordinary temperature. Almost immediately the silver began to darken in color from the lower edge of the gauze upwards. When this ceased, the decomposition was assumed to be at an end, whereupon the gauze was raised from the solution, rinsed with water and further washed with alcohol and ether. It was weighed after drying for a short time. For the gauze, a platinum spiral was substituted in the residual liquor in the beaker; the current was reversed, the layer of mercury being made the anode, when the sodium was rapidly driven into the water. All this occupied about twenty minutes, after which the alkaline liquor was titrated with standardized acid.

[1] *Ztschr. Electrochem.*, **1**, 137; **2**, 169.
[2] *Ztschr. Electrochem.*, **4**, 539.

A solution of salt, containing 0.0606 gram of chlorine and 0.0390 gram of sodium, gave:

Number.	Cl. Gram.	Na. Gram.
1	0.0606	0.0389
2	0.0610	0.0384

Six hours were allowed for the decomposition. The current showed 0.0325 to 0.03 ampere and 2 volts.

On electrolyzing a solution of barium chloride, in the same way, there were obtained

Ba. Per cent.	Cl. Per cent.		Ba. Per cent.	Cl. Per cent.
55.87	28.69	instead of	56.14	29.09
56.07	29.31		....	....

Strontium bromide was analyzed with just as much success. The same is true of other halides. Perhaps it may be well to add that both sodium chloride and barium chloride were electrolyzed successfully without the use of the mercury cathode. A flat, platinum spiral was made to take its place. The alkaline liquor, observing proper current conditions, did not interfere with the deposition of the halogen upon the silver gauze. The thought occurred that in this behavior there was a method of preparing caustic if only some other metal than silver could be applied as anode to take up the chlorine. Numerous experiments in this direction were made, but they resulted negatively.

In this work the writer had the aid of Messrs. William Blum, Raymond Wells, W. M. Howard, and Claude Poole, to each of whom his thanks are here expressed.

In conclusion it may be remarked that the hints which have been developed by this use of a mercury cathode are numerous. The separations of iron from uranium, titanium, zirconium and thorium point to other possibilities where this metal is separated with difficulty, more especially the rare earth metals. Further, there is a noticeable difference in the decomposition pressure of bromides of the alkaline earth metals, so that it would seem as if in a mixture of them this method would yield sharper determinations than we are by force of circumstances obliged to accept. The analysis of barium chloride or of common salt in the electrolytic way was not dreamed of in the years of the development of electrochemical analysis. In 1865 the metal copper was first determined electrolytically. Since then many other metals have been brought

into the circle of experimentation, but it is only now in the present—a period nearly forty years later—that interest is being taken in the determination of acidulous groups by the help of the current. To the writer, the possibilities that suggest themselves with other halides than those of the alkali and the alkaline earth metals seem great, and it is his hope that he may be permitted to continue studies in this direction for a little while longer.

UNIVERSITY OF PENNSYLVANIA.

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METAL SEPARATIONS IN THE ELECTROLYTIC WAY.

BY EDGAR F. SMITH.

Received June 26, 1903.

THE purpose of this communication is to submit the results obtained in trying to effect the separation of silver, mercury and copper from selenium and tellurium. These gaps in electrochemical analysis existed with two exceptions, *viz.*, silver from selenium, and copper from tellurium, and as the separations were needed both for practical reasons and also to extend and complete the possible range of applicability of the current in analysis, they were tried with evident success, as shown in the sequel.

SILVER FROM SELENIUM.

(*a*) *In Alkaline Cyanide Solution.*—In the *Zeitschrift für anorganische Chemie*, 31, 393 and This Journal, 25, 225, appeared Meyer's account of a method of determining the atomic weight of selenium, which consisted in electrolyzing silver selenite in cyanide solution. The results were so very concordant that there can be little question as to the completeness of the separation of the two metals. Working conditions were not given by Meyer, hence it was thought advisable to give those which in this laboratory proved very satisfactory for this particular separation. They appear in the following lines:

Silver present	0.1341 gram.
Sodium selenate present	0.2500 gram.
Potassium cyanide	3 grams.
Total dilution	150 cc.
$N.D_{100}$	0.02 ampere.
Pressure	2.5 volts.
Temperature	60° C.
Time	6 hours.
Silver found	0.1333 gram.

In another trial, with conditions like those just described, the silver which was precipitated weighed 0.1334 gram. These slight differences from the required amount of metal seemed to show that perhaps the current might well be increased toward the end of the experiment. This was done in two instances, from 0.03 ampere and 2.5 volts to 0.05 ampere and 3.5 volts. In consequence, the precipitated silver weighed 0.1340 gram instead of 0.1341 gram; further, the period of precipitation was reduced to three hours. The deposit of silver was pure white in color. The washing and drying were performed as so frequently mentioned in former accounts of silver determinations, and the details need not be given here.

(*b*) *In Nitric Acid Solution.*—The separation proving to be most satisfactory in an alkaline cyanide solution, the next step was to ascertain what would result in conducting it in the presence of an acid. The following conditions prevailed:

Silver present	0.1341 gram.
Sodium selenate present	0.2500 gram.
Nitric acid (sp. gr. 1.43)	1 cc.
Total dilution	150 cc.
$N.D_{100}$	0.015 ampere.
Pressure	1.25 to 2 volts.
Temperature	60° C.
Time	3 hours.

The silver deposit weighed 0.1342 gram. It was perfectly adherent and crystalline in appearance.

SILVER FROM TELLURIUM.

(*a*) *In Alkaline Cyanide Solution.*—It was believed that no difficulty would be met in making this separation with conditions similar to those pursued with silver from selenium in the same electrolyte. They were therefore tried. The precipitation of the silver proceeded very satisfactorily for an hour or more, then the deposit commenced to grow dark in color, and very soon black flakes appeared as a scum on the surface of the liquid and on the deposit as well. This behavior was always noticed, so that the efforts in this direction were abandoned. The attempt to separate mercury and copper from tellurium in cyanide solutions also resulted negatively. As will be observed below, their separation from selenium was most successful. By analogy, it would be expected that if silver, mercury and copper could be separated from

selenium in an alkaline cyanide bath, their separation from tellurium probably ought to follow as well under similar conditions. Here it did not. It is only another instance of cases where experiment alone can give the true answer.

(*b*) *In Nitric Acid Solution.*—

Silver present	0.1341 gram.
Sodium tellurate present	0.1344 gram.
Nitric acid (sp. gr. 1.43)	1 cc.
Dilution	150 cc.
$N.D_{100}$	0.01 to 0.015 ampere.
Pressure	1.25 to 2.0 volts.
Temperature	60° C.
Time	3 ½ hours.

The white crystalline deposit weighed 0.1344 gram.

In a second trial with like conditions the precipitated silver weighed 0.1341 gram.

MERCURY FROM SELENIUM.

(*a*) *In Alkaline Cyanide Solution.*—The example which follows demonstrated the applicability of the method:

Mercury present	0.1272 gram.
Sodium selenate present	0.2500 gram.
Potassium cyanide	1 gram.
Dilution	150 cc.
$N.D_{100}$	0.03 ampere.
Pressure	3 volts.
Temperature	60° C.
Time	5 to 6 hours.
Mercury found	0.1276 gram.

(*b*) *In Nitric Acid Solution.*—The conditions observed in the separation of silver from selenium will give most satisfactory results here.

MERCURY FROM TELLURIUM.

As previously observed, this electrolytic separation is not possible in an alkaline cyanide solution. It only remained, therefore, to ascertain whether it could be performed in a nitric acid solution. The trials were successful. One example will suffice to illustrate the most favorable conditions:

Mercury present	0.1272 gram.
Sodium tellurate present	0.2500 gram.
Nitric acid (sp. gr. 1.43)	3 cc.
Dilution	150 cc.

$N.D_{100}$	0.04 to 0.05 ampere.
Pressure	2 to 2.25 volts.
Temperature	60° C.
Time	5 hours.
Mercury found	0.1276 gram.

COPPER FROM SELENIUM.

(*a*) *In Alkaline Cyanide Solution.*—Two trials were made with conditions as follows:

Copper present	0.0745 gram.
Sodium selenate present	0.2500 gram.
Potassium cyanide	1 gram.
Dilution	150 cc.
$N.D_{100}$	0.2 ampere.
Pressure	3.5 to 4 volts.
Temperature	60° C.
Time	5 hours.
Copper found	(*a*) 0.0745 gram. (*b*) 0.0742 gram.

(*b*) *In Nitric Acid Solution.*—Just as in previous cases, all the results will not be given here. The conditions which proved most satisfactory were these:

Copper present	0.0745 gram.
Sodium selenate present	0.2500 gram.
Nitric acid (sp. gr. 1.43)	1 cc.
Dilution	150 cc.
$N.D_{100}$	0.05 to 0.08 ampere.
Pressure	2 to 2.5 volts.
Temperature	65° C.
Time	4 hours.
Copper found	(*a*) 0.0747 gram. (*b*) 0.0738 gram.

(*c*) *In Sulphuric Acid Solution.*—The quantities of copper and selenium present were the same as in the preceding separations. One cc. of concentrated sulphuric acid was added and the solution was electrolyzed with $N.D_{100} = 0.05$ to 0.10 ampere and 2 to 2.25 volts at a temperature of 65° C. The precipitated copper weighed 0.0743 gram instead of 0.0745 gram. The precipitation was finished in less than six hours.

COPPER FROM TELLURIUM.

The separation of these metals in cyanide solution, as already observed, failed. In nitric acid solution, they have been separated with perfect satisfaction.[1] It remained, therefore, to give the condi-

[1] Smith's "Electrochemical Analysis," 3rd edition, p. 134.

tions under which the two were separated with ease in the presence of sulphuric acid.

Copper present	0.0745 gram.
Sodium tellurate present	0.2000 gram.
Concentrated sulphuric acid	1 cc.
Dilution	150 cc.
$N.D_{100}$	0.05 to 0.1 ampere.
Pressure	2 to 2.25 volts.
Temperature	65° C.
Time	6 hours.
Copper found	(*a*) 0.0747 gram. (*b*) 0.0748 gram.

The writer has had the assistance of Mr. S. H. Ross in working out the details of these experiments, for which he would here acknowledge his indebtedness.

UNIVERSITY OF PENNSYLVANIA.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, NO. 72.]

THE RAPID PRECIPITATION OF METALS IN THE ELECTROLYTIC WAY.[1]

BY FRANZ F. EXNER.

Received July 5, 1903.

SEVERAL years ago experiments were made in this laboratory looking to the electrolytic separation of molybdenum from tungsten. The anode was made to rotate by means of a small electric motor,[2] the idea being to use high currents with a high speed of rotation of the anode, thus hastening the deposition and, by agitation of the electrolyte, overcoming certain disturbances which had arisen. In the particular case referred to, the results were not entirely satisfactory. The idea, however, was shortly after tried upon other metals with success and led to the present investigation. Klobukow[3] called attention to the agitation of the electrolyte, but never published any results. Gooch and Medway[4] recently described successful experiments made with copper, nickel and silver solutions by *rotating the cathode.*

The purpose of the present investigation was to note the results

[1] From the author's thesis for the Ph.D. degree.

[2] Smith's "Electrochemical Analysis," p. 77, third edition, 1902.

[3] *J. prakt. Chem.*, **33**, 475; **40**, 121.

[4] *Am. J. Sci.* [4], **15**, 320.

following the *rapid rotation of the anode* and to develop with care the conditions for successful work, in various electrolytes,[1] for a number of metals. The result has been that many of them can now be precipitated quantitatively by the current in such astonishingly short periods that the methods of electrolysis are made more available to the analyst than heretofore. The essentials are recorded in the paragraphs which follow and the reader is referred to the author's thesis for greater details.

An ordinary platinum dish was used as cathode. The anode was a spiral of heavy platinum wire. It was 2 inches in diameter. Its center was depressed to give it the form of a shallow bowl. It was usually made to perform from 500 to 600 revolutions per minute. At higher speeds, the electrolyte is thrown against the cover-glasses; this is not objectionable, unless the dish contains too much liquid. The solution may sweep around the edge of the dish under the cover-glasses throughout the entire operation without any loss. The volume of liquid never exceeded 125 cc. and was not less than 110 cc. In every case the electrolyte was heated almost to boiling before exposing it to the action of the current. No external heat was applied during the electrolysis. The high currents kept the liquid hot. When the decomposition was finished, the rotator was stopped and the current was reduced by the introduction of resistance, water being added to cover the exposed metal, thus preventing its oxidation. The liquid in the dish was siphoned off, the dish being kept full by the addition of water from a wash-bottle. The metallic deposit was washed and dried in the customary way.

EXPERIMENTAL PART.

Copper.—This metal was precipitated from these solutions: A, sulphuric acid; B, nitric acid; C, ammonium sulphate and ammonia; D, ammonium nitrate and ammonia; E, potassium cyanide. The results were as follows:

A

No. of exp.	$CuSO_4$ = Cu. Gram.	H_2SO_4 dil. 1 : 10. cc.	Current $N.D_{100}$ = A.	V.	Time. Minutes.	Deposited Cu. Gram.	Error. mg.
1	0.4994	1	3	15	3	0.4992	0.2
			4	15	2		
			5	14–9	5		
2	"	1	5	"	5	0.4994	"
3	"	1	5	"	5	0.4994	"

[1] Consult Smith's "Electrochemical Analysis," 3rd edition, 1902.

[2] The brace indicates that all those current conditions were used in the experiment acording to the time given.

B.

No. of exp.	$CuSO_4$ = Cu. Gram.	Conc. HNO_3. cc.	Conc. NH_4OH sol. cc. After 10 min.	Current $N.D_{100}$ = A.	V.	Time. Minutes.	Deposited Cu. Grams.	Error. mg.
1	0.2484	1.0	....	5	10	10	0.2385	—9.9
2	0.2484	1.0	....	5	10	15	0.2387	—9.7
3	0.2484	1.0	....	5	10	20	0.2393	—9.1
4	0.2484	0.5	....	5	12	10	0.2482	—0.2
			5	3	18	5		
5	0.2484	1.0	....	5	10	10	0.2483	—0.1
			5	5	12	5		
6	Identical with 5.							
7	0.4968	1.0	....	5	8	10	0.4964	—0.4
			5	5	10	5		

In Experiments 4 to 7, the electrolysis was first conducted for ten minutes in a nitric acid solution and then 5 cc. of concentrated ammonia water were added. This caused a change in the resistance of the solution, especially when only 0.5 cc. of nitric acid was used. The change was less marked when 1 cc. of the nitric acid was added, and since it also gave better results, that quantity is to be preferred. The deposit from this electrolyte was very satisfactory. It was dense, bright, and metallic in appearance.

C.

No. of exp.	$CuSO_4$ = Cu. Gram.	$(NH_4)_2SO_4$. Grams.	Conc. NH_4OH. cc.	Current $N.D_{100}$ = A.	V.	Time. Minutes.	Deposited Cu. Gram.	Error. mg.
1	0.2484	3	20	5	8	5	0.2488	+0.4
2	0.2484	1	20	5	12	5	0.2488	+0.4
3	0.4968	1.5	30	5	12	8	0.4966	—0.2

The conditions of 2 or 3 are preferable. The deposit is adherent. This electrolyte will be preferred, because in it the least time is required for complete precipitation.

D.

No. of exp.	$CuSO_4$ = Cu. Gram.	NH_4NO_3. Grams.	Conc. NH_4OH solution. cc.	Current $N.D_{100}$ = A.	V.	Time. Minutes.	Deposited Cu. Gram.	Error. mg.
1	0.2484	3.0	20	5	8	10	0.2463	—2.1
2	0.2484	1.0	20	5	12	10	0.2483	—0.1
3	0.4968	1.5	30	5	12	15	0.4968	0.0
4	0.4968	1.5	30	5	12	14	0.4964	—0.4

The conditions of Experiments 2 and 3 are the most desirable. The deposits were excellent in character. A great advantage of this solution is, that in the ordinary course of analysis copper is usually obtained as nitrate. These conditions were made use of in the separation of copper from nickel.

E.

No. of exp.	$CuSO_4$ = Cu. Gram.	KCN.	Current $N.D_{100}$ = A.	V.	Time. Minutes.	Deposited Cu. Gram.	Error. mg.
1	0.2484	Least possible for sol.	5	12	10	0.2136	—34.8
2	0.2484	"	6	18	10	0.2465	— 1.9
3	0.2484	"	6	18	18	0.2479	— 0.5
4	0.2484	"	6	18	18	0.2478	— 0.6

The electrolyte yielded its last traces of copper very slowly, which was probably due to the solvent action of the solution upon the deposit. The deposits were of a golden red color and shone as if they had been polished.

NICKEL.

The solutions used in the following experiments were: A, ammonium sulphate and ammonia; B, acetic acid and ammonia; C, ammonium nitrate and ammonia; D, potassium cyanide.

A.

No. of exp.	$NiSO_4$ = Ni. Gram.	$(NH_4)_2SO_4$. Grams.	Conc. NH_4OH. cc.	Current $N.D_{100}$ = A.	V.	Time. Minutes.	Deposited Ni. Gram.	Error. mg.
1	0.2498	1.5	20	4	12	15	0.2496	—0.2
2	0.4996	1.5	30	5	10	15	0.4977	—1.9
3	0.4996	1.5	25	5	10	17	0.4998	+0.2

The conditions in 1 and 3 are the most desirable. The deposits were gray in color, dense, adherent and thoroughly satisfactory.

B.

No. of exp.	$NiSO_4$ = Ni. Gram.	30 % sol. $HC_2H_3O_2$ cc.	Conc. NH_4OH. cc.	Current $N.D_{100}$ = A.	V.	Time. Minutes.	Deposited Ni. Gram.	Error. mg.
1	0.2498	10	10	5	8.0	10	....	....
2	0.2498	10	25	5	6.5	10	0.2498	....

The conditions in 2 were very satisfactory. The deposits were much like those from electrolyte A.

An experiment was performed in which 3 grams of ammonium nitrate were substituted for the acetic acid in Experiment B, 2; but after ten minutes no deposit had been formed. This suggested a possible separation from copper, which was worked out later. The experiments made with potassium cyanide were abandoned.

ZINC.

A solution of the sulphate was used. The dishes in which the precipitations were made were coated with silver. The electrolytes were: A, sodium acetate and acetic acid; B, sodium hydroxide; C, sodium hydroxide and potassium cyanide.

A.

No. of exp.	$ZnSO_4$ = Zn Gram.	$NaC_2H_3O_2$ Grams.	$HC_2H_3O_2$ 30 per cent. solution. cc.	Current $N.D_{100}$ = A.	V.	Time. Minutes.	Deposited Zn. Gram.	Error. mg.
1	0.2502	1	0.2	3	18	10	0.2502	...
2	0.2502	3	0.2	4	15	10	0.2502	—0.2
3	0.5004	3	0.2	4	18	15	0.5001	—0.3
4	0.5004	3	0.2	4	10	15	0.5002	—0.2
5	0.5004	1	0.2	4	19	15	0.5000	—0.4

Experiments 1 and 5 show that 1 gram of sodium acetate requires too high a voltage to overcome the resistance, causing an undue amount of heat. The high voltage in Experiment 3 was due to the great speed of rotation. The latter was reduced to 600 revolutions per minute in Experiment 4. The conditions in Experiment 2 and 4 are to be preferred, and gave very satisfactory results. The deposits were light gray in color, and crystalline.

B.

No. of exp.	$ZnSO_4$ = Zn. Gram.	NaOH. Grams.	Current $N.D_{100}$ = A.	V.	Time. Minutes.	Deposited Zn. Gram.	Error. mg.
1	0.5004	7	5	5	15	0.5003	—0.1
2	0.5004	5	5	6	15	0.5003	—0.1
3	0.5004	8	5	5	15	0.5004	...
4	0.5004	12	5	5	15	0.5006	+0.2

Nothing is gained by the extra sodium hydroxide in Experiment 4. The conditions of Experiment 3 were most satisfactory. The deposit from this electrolyte was sufficiently adherent for washing and weighing. C. Two experiments were made in which the zinc sulphate solution was precipitated by sodium hydroxide, the precipitate redissolved in potassium cyanide, and electrolyzed in the usual way, but it was finally found necessary to abandon this electrolyte.

SILVER.

The only electrolyte tried was the cyanide. A speed of 700 revolutions per minute was found to be most satisfactory.

No. of exp.	$AgNO_3$ = Ag. Gram.	KCN. Grams.	Current $N.D_{100}$ = A.	V.	Time. Minutes.	Deposited Ag. Gram.	Error. mg.
1	0.2495	2	2	5	7	0.2492	+0.2
2	0.4990	2	2	5	10	0.4990	. .
3	0.4990	2	2	5	9	0.4992	+0.2

The silver came down as a dense white deposit, excepting the last traces, which were a little loose, but quite adherent.

BISMUTH.

This metal proved most troublesome. The speed of rotation employed varied from 700 to 900 revolutions per minute. Electrolyte: 0.5510 gram of bismuth dissolved in a small excess of nitric acid and electrolyzed with a current $N.D_{100} = 1$ A. $V = 2.5$. Time = 18 minutes. The deposit of bismuth weighed 0.5507 gram. It was white and crystalline at first, but later it became black and loose, yet sufficiently adherent for washing and weighing.

Ten different electrolytes were tested with current strengths varying from 4 to 5 amperes, but all gave more unsatisfactory results than when nitric acid alone was present. The only electrolyte that gave deposits sufficiently satisfactory for analysis was that containing a small excess of nitric acid.

The suggestion of Vortmann was then applied, and the bismuth deposited with mercury as an amalgam. Solutions of mercurous nitrate and bismuth nitrate, each dissolved in the smallest excess of nitric acid, were used.

No. of exp.	$Bi(NO_3)_3$ = Bi. Gram.	$HgNO_3$ = Hg. Gram.	Conc. HNO_3. cc.	Current $N.D_{100}$ = A.	V.	Time. Minutes.	Deposited Bi. Gram.	Error. mg.
1	0.2970	0.2920	..	4	12	15	0.2965	—0.5
2	0.2970	0.2920	..	4	12	12	0.2967	—0.3
3	0.2970	0.2920	1	5	8.5	8	0.2972	+0.2
4	0.2970	0.2920	1	5	8.5	8	0.2971	+0.1

The 1 cc. of nitric acid lowered the voltage and better results followed. The conditions of Experiments 3 and 4 are to be preferred. The deposit was iron-gray in color and very satisfactory.

MERCURY.

A solution of mercurous nitrate containing nitric acid was used. The speed of rotation was 700 revolutions per minute.

No. of exp.	$HgNO_3$ = Hg. Gram.	Conc. HNO. cc.	Current $N.D_{100}$ = A.	V.	Time. Minutes.	Deposited Hg. Gram.	Error. mg.
1	0.2920	1	4	11	15	0.2920	..
2	0.2920	1	7	12	5	0.2919	—0.1
3	0.5840	1	7	12	7	0.5837	—0.3

The deposits were perfect mirrors of pure mercury, and dissolved off the dish with great ease. The loss in weight of the dish in these three experiments was only 0.6 milligram.

COBALT.

A solution of cobalt sulphate was used. The speed of rotation

was 700 revolutions per minute. The electrolytes were: A, ammonium sulphate and ammonia; B, sodium and ammonium acetates and ammonia.

A.

No. of exp.	$CoSO_4$ = Co. Gram.	$(NH_4)_2SO_4$. Grams.	Conc. NH_4OH sol. cc.	Current. $N.D_{100} = A.$	V.	Time. Minutes.	Deposited Co. Gram.	Error. mg.
1	0.2460	3	50	5	10	15	0.2433	—2.7
2	0.2460	3	50	5	10	17	0.2440	—2.0

The solution from Experiment 2 gave no test for cobalt with ammonium sulphocarbonate, but there was a small deposit upon the anode. Experiments to remedy the defects of this electrolyte were not carried out.

B.

No. of experiment.	$CoSO_4$ = Co. Gram.	30 per cent. solution $HC_2H_3O_2$ cc.	$NaC_2H_3O_2$. Grams.	Concentrated NH_4OH. cc.	Current $N.D_{100} = A.$	V.	Time. Minutes.	Deposited Co. Gram.	Error. mg.
1	0.2460	10	.	60	5	8	16	0.2404	5.6
2	0.2460	5	5	60	5	12 to 8	15	0.2462	+0.2
3	0.2460	.	2	60	5	15 to 12	15	0.2462	+0.2
4	0.2460	5	1	50	5	12 to 9	17	0.2459	—0.1
5	0.2460	5	1	50	5	10 to 7	15	0.2459	—0.1
6	0.4920	5	1	50	5	9 to 8	22	0.4916	—0.4
7	0.4920	5	1	50	5	9 to 8	22	0.4917	0—0.3

In Experiment 1 the deposit was excellent, but there was oxide on the anode.

The deposit in Experiment 2 was very good, but there was a slight discoloration of the anode.

The deposit of Experiment 3 was satisfactory. The anode was not coated.

The deposits in Experiments 4 to 7 were good. They were gray in color and quite metallic in appearance. The discoloration of the anode was so slight as to be negligible.

In the last three experiments, the speed was 500 revolutions per minute. These conditions are recommended. Sodium acetate hastens the deposit and prevents deposition upon the anode, while the ammonium acetate improves the deposit, but retards its formation.

CADMIUM.

The following electrolytes were used: A, sulphuric acid; B,

sodium acetate and potassium sulphate; C, potassium cyanide. The speed of rotation was about 600 revolutions per minute.

A.

No. of exp.	$CdSO_4$ = Cd. Gram.	H_2SO_4 dil. 1 : 10. cc.	Current $N.D_{100}$ = A.	V.	Time. Minutes.	Deposited Cd Gram.	Error. mg.
1	0.2756	3	5	9	10	0.2756	....
2	0.2756	1	5	17–11	10	0.2755	—0.1
3	0.5512	1	5	8	15	0.5508	—0.4

Deposit 1 was crystalline at first, but the last portions of metal came down loose, but sufficiently adherent. Deposits 2 and 3 were beautifully crystalline and very satisfactory.

B, *Experiment 1.*—Electrolyte: Cd = 0.5512 gram. Sodium acetate = 2 grams. Potassium sulphate = 0.5 gram. Current $N.D_{100}$ = 5 A. V = 12. Time = 15 minutes. The deposited cadmium weighed 0.5514 gram. The potassium sulphate was added to increase the conductivity of the electrolyte.

Experiment 2.—Electrolyte: Cd = 0.5512 gram. It was precipitated with 0.5 gram of sodium hydroxide, the precipitate was dissolved with acetic acid, and 0.5 gram of potassium sulphate added. Current $N.D_{100}$ = 5 A. V = 11. Time = 15 minutes. Deposited Cd = 0.5514 gram.

C.

No. of exp.	$CdSO_4$ = Cd. Gram.	NaOH. Grams.	KCN. Grams.	Current $N.D_{100}$ = A.	V.	Time. Minutes.	Deposited Cd. Gram.	Error. mg.
1	0.5530	5	2	5	8	15	0.5531	+0.1
2	0.5530	5	2	5	8	10	0.5528	—0.2
3	0.5530	5	2	5	8	12	0.5528	—0.2
4	0.5530	5	2	5	8	10	0.5530	....

The deposits were white, compact and very satisfactory.

IRON.

A solution of ferric ammonium sulphate with ammonium oxalate was used as electrolyte. The speed of rotation was about 800 revolutions per minute.

No. of exp.	Ferric am. alum = Fe. Gram.	$(NH_4)_2C_2O_4$. Grams.	$H_2C_2O_4$ sat. sol. cc.	Current. $N.D_{100}$=A.	V.	Time. Minutes.	Deposited Fe. Gram.	Error. mg.
1	0.2461	7	1	7	7.4	25	0.2458	—0.3
2	0.2461	7.5	·	7	7.5	25	0.2463	+0.2
3	0.2461	7.5	·	7	7.5	25	0.2461	..
4	0.4922	7.5	·	7	7.5	35	0.4922	..

The deposits were so dense and light in color that they resembled the polished platinum dish.

LEAD.

The metal was deposited as dioxide upon a dish which had its inner surface roughened by a sand blast. Over a gram of deposited dioxide showed no tendency to scale off. The speed of rotation was about 600 revolutions per minute. The only electrolyte used was nitric acid.

No. of exp.	$Pb(NO_3)_2$ = Pb. Gram.	HNO_3 conc. cc.	Current $N.D_{100}$ = A.	V.	Time. Minutes.	Deposited PbO_2. Grams.	Error. mg.
1	0.2807	20	10	4.5	10	0.2804	—0.3
2	0.2807	20	10	4.5	10	0.2804	—0.3
3	0.5614	20	10	4.5	13	0.5613	—0.1
4	0.5614	20	10	4.5	13	0.5614	....
5	1.1228	20	10	4.5	15	1.1228	....

The deposits of lead dioxide were of a uniform, velvety black color.

No success was had with manganese.

MOLYBDENUM.

Electrolyte: A solution of sodium molybdate containing 0.2250 gram of molybdenum trioxide was placed in the dish, and to this were added 2 cc. of sulphuric acid (dilute 1 : 10), and 1 gram of potassium sulphate. The current $N.D_{100} = 4$ A. $V = 15$. Time = 20 minutes. The molybdenum trioxide found weighed 0.2246 gram. The speed of the anode equaled 300 to 400 revolutions per minute.

TIN.

The electrolyte in this instance was a freshly prepared solution of stannous ammonium chloride, to which ammonium oxalate was added. The speed of the anode equaled 300 revolutions per minute.

No. of exp.	$SnCl_2$. $2NH_4Cl$ = Sn. Gram.	$(NH_4)_2C_2O_4$ hot sat. sol. cc.	Current. $N.D_{100}$=A.	V.	Time. Minutes.	Deposited Sn. Grams.	Error. mg.
1	0.5396	100	5	5	13	0.5392	—0.4
2	0.2193	100	5	5.5	15	0.2193	....
3	0.2193	100	5	5.5	15	0.2191	—0.2
4	0.2193	100	5	5.5	15	0.2191	—0.2
5	0.2193	100	5	5.5	15	0.2193	....
6	0.4355	100	5 8	5.5 6.5	15[1] 3	0.4353	—0.2
7	0.4355	100	5 8	5.5 6.5	15 5	0.4355	....
8	1.0800	100	5	4.5	20	1.0801	+0.1

[1] In Experiments 6 and 7 the brace indicates two current conditions. The 5-A current running 15 minutes after which it was changed to 8-A.

GOLD.

The electrolyte was a solution of gold chloride to which potassium cyanide was added. The speed of rotation was about 500 revolutions per minute.

No. of exp.	$AuCl_3$ = Au. Gram.	KCN. Grams.	Current $N.D_{100}$ = A.	V.	Time. Minutes.	Deposited Au. Gram.	Error. mg.
1	0.0290	1.0	5	11	10	0.0289	0.1
2	0.0725	2.0	5	11	10	0.0725	...
3	0.1450	1.5	5	11	7	0.1447	—0.3

The deposits were excellent.

ANTIMONY.

Antimony chloride, with just enough hydrochloric acid to keep it in solution, was mixed with sodium hydroxide, sodium hydrosulphide and potassium cyanide, then electrolyzed as indicated below. The speed of rotation of the anode was 400 to 500 revolutions per minute.

No. of exp.	$SbCl_3$ + HCl = Sb Gram.	NaOH 10 % sol. cc.	NaHS. cc.	KCN. Grams.	Current $N.D_{100}$ = A.	V.	Time. Minutes.	Deposited Sb. Gram.	Error. mg.
1	0.3042	30	20	2	5	4.5	20	0.3042	...
2	0.3042	30	20	2	5	4.5	20	0.3041	—0.1
3	0.3042	30	20	2	5	4.5	18	0.3041	—0.1

The deposits under these conditions were excellent. They showed a dense, light, metallic appearance. This is a new electrolyte for antimony.

No success was had with the deposition of arsenic.

SEPARATIONS.

SEPARATION OF COPPER FROM NICKEL.

The sulphates of the metals were used. The speed of rotation was about 600 revolutions per minute.

No. of experiment.	$CuSO_4$ = Cu. Gram.	$NiSO_4$ = Ni. Gram.	Concentrated HNO_3 cc.	NH_4NO_3. Grams.	Current $N.D_{100}$ = A.	V.	Time. Minutes.	Deposited Cu. Gram.	Error. mg.
1	0.2457	0.25	0.25	3	4	5	15	0.2460	+0.3
2	0.2457	0.25	0.25	3	4	5	15	0.2458	+0.1

The deposits of copper were good and free from nickel. Several other experiments were performed in which more free nitric acid was used, and some in which less time was allowed, but in all of

them the precipitation was incomplete. The separation is probably possible, also, in an ammonia solution in the presence of ammonium nitrate.

Analysis of Nickel Coin.

A nickel coin, weighing 4.8514 grams, was dissolved in nitric acid, then evaporated on the water-bath, and the crystallized residue dissolved in water. Twenty-five cc. of this solution were placed in a weighed platinum dish and 3 grams of ammonium sulphate, and 1 gram of ammonium nitrate added. This solution was diluted with water to 125 cc., heated nearly to boiling and electrolyzed with a current of $N.D_{100} = 5$ A. $V = 5$. Time = 20 minutes. The precipitated copper weighed 0.3629 gram, equal to 74.81 per cent. of the coin. The solution from this deposit was precipitated with sodium hydroxide and bromine water, and the precipitate filtered, washed and dissolved in dilute sulphuric acid, containing 2.5 cc. of concentrated acid. To this solution 30 cc. of concentrated ammonia water were added, the whole diluted to 125 cc., heated, and electrolyzed with a current of $N.D_{100} = 6$ A. $V = 5$. Time = 17 minutes. The deposited nickel weighed 0.1185 gram, corresponding to 24.42 per cent. of the coin.

The attempt was next made to see how quickly a complete analysis of a nickel coin could be made. This was done as follows:

Weight of coin = 4.925 grams.

It was dissolved in 20 cc. of concentrated nitric acid diluted with an equal volume of water. When the solution was complete, the liquid was exactly neutralized with ammonia, transferred to a 250 cc. measuring flask and this filled with water to the mark. 25 cc. of this liquid were then transferred to a weighed platinum dish and 3 grams of ammonium sulphate were added. This was diluted to 125 cc., heated and electrolyzed with a current of $N.D_{100} = 5$ A. $V = 5.5$ for 20 minutes. The precipitated copper weighed 0.3691 gram = 74.95 per cent. of the coin. The solution from the copper was precipitated with sodium hydroxide and bromine water, filtered and washed. The precipitate was then dissolved in 2 cc. of concentrated sulphuric acid diluted with water, 30 cc. of concentrated ammonia water added, diluted to 125 cc., heated, and the solution electrolyzed with a current of $N.D_{100} = 6$ amperes and 5 volts. Twenty minutes were required for the deposition. The precipitated nickel weighed 0.1217 gram, corresponding to 24.71 per cent. The solution from the nickel deposit was

filtered, and the precipitate washed, ignited and weighed. The weight of ferric oxide was 0.0026 gram, which is equivalent to 0.35 per cent. of metallic iron. The total percentage equalled 100.01. The time required for the complete analysis was two and a half hours.

SEPARATION OF COPPER FROM ZINC.

The conditions which served for the separation of copper from nickel are applicable in its separation from zinc.

No. of exp.	$CuSO_4$ = Cu. Gram.	$ZnSO_4$ = Zn. Gram.	NH_4NO_3. Grams.	Conc. HNO_3. cc.	Current. $N.D_{100}$ = A.	V.	Time. Minutes.	Deposited Cu. Gram.	Error. mg.
1	0.2457	0.25	3	0.25	5	9	15	0.2458	+0.1
2	0.2457	0.25	3	0.25	5	9	15	0.2460	+0.3

This is sufficient to show the possibilities of this method of analysis. At the present time other separations are in progress.

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[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES, COLUMBIA UNIVERSITY, NO. 84.]

THE VOLUMETRIC DETERMINATION OF BISMUTH AS MOLYBDATE AND ITS SEPARATION FROM COPPER.[1]

BY HERMAN S. RIEDERER.

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AT THE present time the quantitative determination of bismuth is conducted in the great majority of cases by precipitation as bismuth basic carbonate by ammonium carbonate, in spite of the fact that many different schemes have been published for its separation from other metals and determination, using other reagents.

It was with the intention of finding, if possible, a reliable volumetric method equal in accuracy to the carbonate method, that this work was undertaken.

As the work progressed and the molybdate method was to be applied to ores, to show its practical value, it developed that a shorter and simpler separation of bismuth from copper, especially, would make the method complete from the ore, and it was then that the precipitation of bismuth with hydrogen sulphide from a solution containing tartaric acid and made alkaline with

[1] From author's thesis for the degree of Doctor of Philosophy. Read at the December meeting of New York Section of the American Chemical Society.

caustic potash and potassium cyanide was worked out and found satisfactory.

EXPERIMENTAL.

For the experimental part of this work a bismuth nitrate solution was prepared and standardized by the following methods: (*a*) Direct evaporation to dryness of a measured volume and ignition of the dry nitrate to trioxide; (*b*) precipitation of basic carbonate, drying and igniting to trioxide. The results obtained by these two methods were further checked by precipitating the bismuth as sulphide, and carefully igniting this to the trioxide (*c*).

(*a*) DIRECT EVAPORATION METHOD.

RESULTS.

$Bi(NO_3)_3$ taken. cc.	Character of vessel used.	Found. Bi_2O_3. Gram.	Found. Bi. Gram.
5	porcelain.	0.0643	0.05765
5	"	0.0643	0.05765
6	"	0.0773	0.06931
20	platinum	0.2578	0.23084
30	"	0.3663	0.34636

(*b*) CARBONATE METHOD.

RESULTS.

$Bi(NO_3)_3$ taken. cc.	Found. Bi_2O_3. Gram.	Found. Bi. Gram.
20	0.2581	0.23140
20	0.2577	0.23106
20	0.2570	0.23042
25	0.3222	0.28888
30	0.3869	0.34689
10	0.1288	0.11548
11	0.1415	0.12687
12	0.1542	0.13826

(*c*) SULPHIDE METHOD.

RESULTS.

$Bi(NO_3)_3$ taken. cc.	Found. Bi_2O_3. Gram.	Found. Bi. Gram.
20	0.2575	0.23086
20	0.2578	0.23114

From these results the strength of the solution was taken to be 1 cc. = 0.01155 gram bismuth.

ELECTROLYTIC METHODS.

It was deemed advisable to try some of the proposed methods

and that of Wimmenauer[1] looked promising. No satisfactory results could be obtained by it, however. Kammerer's[2] method was also tried with no better results, although Smith states in his book that it is probably the best of the proposed methods.

OXALATE METHODS.

Warwick and Kyle[3] proposed, apparently as a new method, the precipitation of bismuth as oxalate either with ammonium oxalate or oxalic acid, and heating to facilitate the reaction. The clear solution is then decanted, and the precipitate is boiled with successive portions of water to convert the precipitate to the basic oxalate. This is then dissolved in acid and the oxalic acid is titrated with standard potassium permanganate solution. Both ammonium oxalate and oxalic acid precipitate bismuth as oxalate, which, however, is easily soluble in excess of ammonium oxalate whether hot or cold. Owing to this fact, ammonium oxalate was not further tried in determining the value of the proposed method. Oxalic acid was then tried as described by Warwick and Kyle.

It was noted that this is nearly an exact copy of Muir's method.[4] The only great difference between them is that in Muir's method the precipitation is done in the cold, while Warwick and Kyle make their precipitation by heating, and also claim that two boilings with 50 cc. of water suffice to convert all the precipitate to the basic salt, while Muir says to boil with successive portions of water till the filtrates are free from acid. In the following experiments it was found that only very small amounts of oxalate could be converted by two boilings, while 0.0924 gram bismuth required three and four boilings with 80-100 cc. water to remove all free acid. The results in the following table were obtained by the factor calculated as given in the method by Warwick and Kyle. If 1 cc. of potassium permanganate equals 0.010 gram iron, it is equivalent to 0.0186 gram bismuth. One cc. of potassium permanganate used was equal to 0.005612 gram iron and hence equivalent to 0.01048 gram bismuth. This was the factor used. To show the irregularity of the results, the last column in the table shows what the factor for potassium permanganate to bismuth would be in each case according to the results obtained.

[1] *Ztschr. anorg. Chem.*, **27**, 1 (1901).

[2] "Electrochemical Analysis," Smith, 3rd edition (1902), p. 67; This Journal, **25**, 83 (1903).

[3] *Eng. and Min. J.*, April, 1901.

[4] *J. Chem. Soc.* (London), **33**, 70 (1878).

RESULTS.

$Bi(NO_3)_3$ taken. cc.	Bi taken. Gram.	$KMnO_4$ used. cc.	Bi found. Gram.	Calculated factors.
4	0.0451	3.8	0.0398	0.01186
6	0.0693	5.6	0.0587	0.01237
8	0.0924	8.4	0.0878	0.01100
10	0.1155	9.6	0.1006	0.01203
12	0.1386	12.4	0.1300	0.01117

These results being irregularly low, the cause was sought in the solubility of the oxalate. It was then found that the bismuth oxalate is slightly soluble in a hot solution containing oxalic acid. Apparently this fact was known to Muir, as in his method the bismuth is precipitated in the cold and the supernatant liquid is decanted. Then the precipitate, free from oxalic acid solution, is converted to the basic oxalate by boiling with water. The method was tried to ascertain its exactness so that it might be used for further standardization, if necessary. The results, however, were irregularly high, due to the difficulty experienced in converting to the basic salt. The precipitate is very fine and heavy and caused violent bumping. Four or more boilings were always necessary to free the washings from oxalic acid. The conversion had not even then been completed.

RESULTS.

$Bi(NO_3)_3$ taken. cc.	Bi taken. Gram.	$KMnO_4$ used. cc.	Bi found. Gram.
4	0.0462	4.6	0.0482
6	0.0693	7.25	0.0775
8	0.0924	10.3	0.1079
10	0.1155	11.7	0.1226
12	0.1386	14 8	0.1551
14	0.1619	16.7	0.1750
8.1	0.0936	9.7	0.1016
9.9	0.1143	11.95	0.1252
4	0.0462	4.35	0.0456
6	0.0693	7.3	0.0765
14	0.1619	16.75	0.1755

In the last three determinations the precipitates were boiled several times after the conversion seemed to be complete, but the amount of oxalic acid retained was still higher than that calculated for the basic oxalate. The method did not seem practical for further work, as three other determinations started with these last three were lost by the violent bumping already mentioned.

Warwick and Kyle also claim that this method is a separation of bismuth from copper, arsenic, antimony and several other

metals. Copper being the most important, its behavior with ammonium oxalate and also oxalic acid was tried and it was found to act like bismuth in both cases, namely, it is soluble in excess of ammonium oxalate and insoluble in oxalic acid. After obtaining these results, it was not thought necessary to test the method of Warwick and Kyle further; as the principle of the method is old, the proposed changes render the method inaccurate, and the separations claimed are impossible.

These conclusions are further confirmed by Grabill,[1] who made a study of the reaction of bismuth with ammonium oxalate. He contradicts Warwick and Kyle, and also states that copper oxalate is insoluble.

Another proof that the separation of bismuth and copper is impossible by oxalic acid is given by the fact that Peters[2] precipitates copper quantitatively with this reagent and determines copper in this way.

THE MOLYBDATE METHOD.

When a solution of ammonium molybdate in nitric acid is added to a nitric acid solution of bismuth nitrate and the whole is neutralized with ammonia but not made alkaline, all the bismuth is precipitated as a molybdate in a fine flocculent form. If this is then warmed without boiling, the whole precipitate will collect into large, heavy flocks which settle very rapidly. This precipitate is easily washed by decantation and filters very rapidly. By the following work it was found that the molybdenum ratio to that of bismuth remains constant.

The limits of the precipitation are very narrow. The ammonium molybdate must be in large excess, three to four times the theoretical amount necessary for combining with all the bismuth. The original solution will contain about 5 per cent. of nitric acid, but this must be almost entirely neutralized with ammonia. To obtain this point, methyl orange is used as an indicator to get the solution neutral, and it is then acidified with 1 or 2 drops of 30 per cent. nitric acid. The whole is then heated on a thick asbestos pad over a small flame until the fine flocks have collected; generally the whole precipitate will rise from the bottom in large masses by the action of the hot circulating solution. The precipitate is then stirred to break it up, after which it is

[1] *Eng. and Min. J.*, **72**, 354 (1901).
[2] *Ztschr. anorg. Chem.*, **26**, 111 (1901).

allowed to settle. The precipitate is exceedingly heavy and settles in a few seconds, forming a compact mass. The supernatant liquid, which must be perfectly clear, is decanted through a plain filter-paper. Then the precipitate is washed twice by decantation with a 3 per cent. solution of ammonium sulphate, after which it is washed on the filter with the ammonium sulphate solution. It is then dissolved in dilute sulphuric acid and run through a Jones reductor with suction; after this, it is strongly acidified with sulphuric acid and is immediately titrated with standard potassium permanganate.[1]

The precipitation and washing were done in a small beaker and the bulk was about 200 cc. It was found best to heat slowly, as with fast heating the solution was liable to come to a boil, which makes the determination unreliable. A 3 per cent. solution of ammonium sulphate was found satisfactory for washing and was preferred to any other salt as it has only constituents of the solution which is run through the reductor, and as ammonium sulphate is inactive to zinc in acid solution and also to potassium permanganate. A reductor with a column of zinc 40 to 45 cm. in length in a tube 1.25 cm. in diameter was used, to avoid the necessity of more than one passage through the zinc, and the suction flask was so large that the titration was made in it directly. Thus air had less chance of reoxidizing the molybdous oxide, which was to be determined by permanganate.

The color of the molybdate precipitate is pure white. Sometimes, when the conditions were not followed exactly, a slightly yellowish to canary-yellow compound resulted which gave varying results, but always lower than the white compound. This yellow molybdate, when formed, could however easily be changed to the white, by first making the solution alkaline with ammonia to throw down bismuth oxyhydrate, and then dissolving this in nitric acid, all this being done in the whole mixture of precipitate and solution. The clear solution is now re-treated as a new solution except that it is not always necessary to add more ammonium molybdate.

The results given in the following tables are calculated for the value in bismuth of 1 cc. of the potassium permanganate solution. To compare the results obtained in this way with an absolute standard, several samples of the purest obtainable bismuth were

[1] For further details of precipitation see the following paper.

weighed out and treated like the standard $Bi(NO_3)_3$ solution with very satisfactory results.

RESULTS.

$Bi(NO_3)_3$ taken. cc.	Bi taken. Gram.	$KMnO_4$ used. cc.	Equivalent amount of bismuth of 1 cc. $KMnO_4$.
9	0.10395	28.5	0.003647
9	0.10395	28.7	0.003621
15	0.17325	47.75	0.003628
16	0.18480	50.9	0.003630
8.5	0.09818	27.	0.003636
12.3	0.14207	30.8	0.004610[1]
7.8	0.09009	24.8	0.003632
9.8	0.11319	31.15	0.003633
11.6	0.13398	30.	0.004466[1]

The results with the yellow precipitates indicate a totally different compound containing more bismuth than the white precipitate.

The following results were obtained with metallic bismuth:

Bismuth taken. Gram.	$KMnO_4$ used. cc.	Value of 1 cc.
0.1100	30.1	0.003654
0.1398	38.3	0.003626
0.1084	29.8	0.003637
0.1434	39.5	0.003630
0.1815	50.0	0.003630

From these results, the value of the potassium permanganate solution was taken as 1 cc. = 0.003630 gram of bismuth.

If the degree of reduction[2] of the molybdenum obtained in a Jones reductor is assumed to correspond to $Mo_{24}O_{37}$, the ratio of bismuth to molybdenum in the white precipitate is 1 : 1.977, while in the yellow precipitates it approaches 1 : 1.5, the ratio for the well-known normal bismuth molybdate.

The ratio was determined gravimetrically as follows: 10 cc. of the bismuth nitrate solution were precipitated as molybdate under the usual conditions. This was decomposed with ammonium sulphide, which precipitated bismuth sulphide and held the molybdenum sulphide in solution. The bismuth sulphide was dissolved with hot, dilute nitric acid, and the bismuth determined by the evaporation method (*a*) as a check on the completeness of precipitation by ammonium molybdate. The molybdenum solution was acidified, saturated with hydrogen sulphide and heated in boiling

[1] Yellow precipitates.

[2] The degree of reduction of the molybdenum and the ratio of bismuth to molybdenum in this precipitate are discussed in the following paper.

water in a pressure bottle. The sulphide was filtered in a weighed platinum, Gooch crucible, washed with dilute sulphuric acid and with alcohol, then ignited very carefully and the oxide MoO_3 weighed. The results were:

	A. Gram.	B. Gram.	C. Gram.
Bi_2O_3 found	0.1289	0.1285	0.1292
MoO_3 found	0.1058	0.1058	0.1057
Atomic ratios, Bi to Mo	1 : 1.985	1 : 1.99	1 : 1.982

These results were obtained on white precipitates; a yellowish precipitate analyzed in the same way gave a ratio of 1 : 1.71.

The ratio of bismuth and molybdenum in the compound having been found to be very nearly 1 : 2, it was evident that some other element or compound entered into the composition of the precipitate. It also showed that this molybdate was unknown in the literature, as the only molybdate of bismuth that could be found was the normal molybdate, ratio 2 : 3, a yellow compound soluble in 500 parts of water.[1] It was naturally supposed that ammonium was the missing factor in the compound, as no other base was employed. Attempts were made to obtain the molybdate pure and free from ammonium sulphate, so that the ammonia in combination could be determined. This was not found possible, as both water and 50 per cent. alcohol decomposed the compound, and no other available liquid could be found with which the ammonium sulphate could be washed out, leaving the pure molybdate behind. This peculiarity of the compound made it necessary to make an indirect determination for ammonia, by finding the total in the compound and combined as sulphate; then determining the sulphuric acid present and calculating its equivalent of ammonia; this subtracted from the total ammonia would give the ammonia in combination. A definite amount of bismuth was employed every time to avoid the necessity of determining this and the molybdenum in each portion.

The results did not check well, but showed conclusively that the precipitate contained ammonia, to the extent of about 1 molecule. Although these results are not sufficiently accurate to prove the formula, they show that the compound is a new bismuth ammonium molybdate with a ratio of bismuth to molybdenum very close to 1 : 2. The formula $BiNH_4(MoO_4)_2$ would satisfy these facts.

It should be emphasized here that the precipitate is pure white;

[1] Storer's "Dictionary of Solubilities."

that if it is yellow it is undoubtedly contaminated by the normal molybdate, and that it is formed when the clear nitric acid solution containing an excess of molybdate is slowly neutralized with dilute ammonia, and then warmed but not boiled. As the conditions for this precipitation are narrow, and the degree of the reduction of molybdenum variable,[1] it is evident that care and strictly uniform conditions are essential to the success of the method.

THE SEPARATION OF BISMUTH AND COPPER.

The exactness of the molybdate method for bismuth having been proved, it was thought advisable to find a shorter separation from copper, so as to make the method of practical value, if possible. The ammonium carbonate method is a perfect separation, if it is repeated several times, in presence of large amounts of copper. Naturally this method is slow.

Pretzfeld,[2] in his new separation of mercury from copper, arsenic, and antimony by hydrogen sulphide in a potassium cyanide solution containing tartaric acid, found that, among a few other metals, bismuth also interferes; he did not, however, determine whether it was completely precipitated. A few experiments showed that all the bismuth was thrown out of solution by Pretzfeld's conditions; namely, the acid solution is neutralized with potassium cyanide after about 30 cc. of a saturated tartaric acid solution have been added; enough potassium cyanide must be added to dissolve any precipitate which may form, except bismuth sulphide thrown out by the sulphur in the cyanide. This alkaline solution is now saturated with hydrogen sulphide gas, and the bismuth sulphide is filtered out. The filtrate is colorless to light lemon-yellow. When copper was added to the bismuth solution and the above conditions were applied, the deep red color mentioned by Pretzfeld was present every time, in spite of the presence of tartaric acid.

When the bismuth copper mixture was first made alkaline with caustic potash, after adding tartaric acid, and potassium cyanide was added till the solution was clear, neither a red color appeared, nor was it necessary to use more than a small amount of potassium cyanide. The solution, even after saturation with hydrogen sulphide was never darker than a light lemon-yellow. The most important points were, however, that all the bismuth was precipi-

[1] See following article.

[2] Dissertation, "The Determination and Separation of Mercury," Columbia University, 1902. This Journal, **25**, 205 (1903).

tated as sulphide in small bulk, all copper remained in solution and the filter-paper could be washed free from copper with potassium cyanide solution or pure water, and pure bismuth sulphide remained.

RESULTS.

$Bi(NO_3)_3$ taken. cc.	Bi taken. Gram.	Cu. Gram.	Bi_2O_3 found. Gram.	Bi found. Gram.
10	0.1155	0.5	0.1285	0.11521
10	0.1155	0.5	0.1287	0.11539
10	0.1155	1.0	0.1284	0.11512

The bismuth sulphide was dissolved in nitric acid, and then the bismuth was reprecipitated as basic carbonate which was ignited to oxide and weighed.

ANALYSIS OF BISMUTH ORES.

Two samples of bismuth ores containing iron, but free from copper, were obtained and these were used to show the exactness of the new method, as compared to the basic carbonate method.

From 0.3 gram to 0.5 gram of the richer ore were used for analysis and treated as follows: The ore was decomposed with nitric acid and was evaporated with sulphuric acid to fumes; after dilution, the residue was filtered off and re-treated with nitric and sulphuric acids as before. The filtrates were combined and diluted to about 750 cc. Then bismuth sulphide was precipitated with hydrogen sulphide and filtered out. For the carbonate method, this sulphide was dissolved in hot dilute nitric acid and precipitated by adding ammonia and ammonium carbonate, and heating. The precipitated basic carbonate was filtered, washed and ignited in a weighed porcelain crucible. To insure against any reduction of metal by the burning of the paper, the carbonate was dissolved through the paper, into the crucible, with hot dilute nitric acid.

For the molybdate method, the bismuth sulphide was also dissolved in nitric acid and this solution was treated with tartaric acid, potassium hydroxide, potassium cyanide and hydrogen sulphide, to free the bismuth of impurities which would interfere in the molybdate method. The pure bismuth sulphide was again dissolved in nitric acid, precipitated as molybdate, dissolved, reduced, and titrated. The following results show the comparative accuracy of the two methods.

RESULTS.

Ore taken. Gram.	Bi_2O_3. Gram.	Bi found. Gram.	Per cent.
0.5001	0.1096	0.0983	19.65
0.5004	0.1098	0.0984	19.67
0.5008	0.1098	0.0984	19.65
0.5009	0.1095	0.0982	19.60

Ore taken. Gram.	$KMnO_4$ used.[1] cc.	Bi found. Gram.	Per cent.
0.5000	29.6	0.0987	19.74
0.3011	17.8	0.0594	19.71
0.3003	17.6	0.0589	19.61

The second ore was similar to the first. The same scheme of analysis was employed.

RESULTS.

Ore taken. Gram.	Bi_2O_3. Gram.	Bi found. Gram.	Per cent.
1.0002	0.0843	0.0756	7.55
0.7506	0.0620	0.0556	7.41

Ore taken. Gram.	$KMnO_4$ used.[1] cc.	Bi found. Gram.	Per cent.
0.7505	17.0	0.0567	7.55
0.5008	11.4	0.0380	7.57

ANALYSIS OF COPPER MATTE CONTAINING BISMUTH.

At the time these analyses were under way, no matte containing bismuth was on hand, so a convenient amount of bismuthinite was mixed and ground up with a matte to make it about 0.5 per cent. to 0.6 per cent. bismuth. This was then analyzed by the two methods, as with the ores.

The method of procedure was similar to that employed in the ores, except that decomposition was effected with nitric and hydrochloric acids, no sulphuric acid being used. For the basic carbonate method the bismuth was precipitated alternately with hydrogen sulphide in acid solution and then with ammonium carbonate in ammoniacal solution to free the bismuth of iron and copper. Otherwise the methods were the same. It may be noted that only one precipitation was necessary for bismuth with hydrogen sulphide in the tartaric acid, potassium hydroxide, and potassium cyanide solution to obtain the bismuth free from copper. For one determination by the molybdate method, the standard permanganate solution was diluted to one-tenth the strength to reduce the error in titration, as the amount of bismuth was so small.

[1] Factor : 1 cc. $KMnO_4$ = 0.003335 gram Bi.

RESULTS.

Matte taken. Gram.	Bi_2O_3 found. Gram.	$KMnO_4$ used. cc.	Per cent.
2.2433	0.0134	...	0.597
2.5295	0.0164	...	0.648
2.0004	0.0126	...	0.565
2.2294	.....	3.9	0.583
2.0032	.....	3.25	0.541
2.0935	.....	3.4	0.542
2.0020	.....	34.2 $\frac{\text{standard}}{10}$	0.553

The molybdate method was applied to the matte in the most unsatisfactory way, as only small samples were used. When, however, enough sample is on hand, in case of a matte low in bismuth, it is advisable to take 5 grams to 10 grams or more to start with, as no difficulty will be experienced in separating the copper, and the quantity of bismuth will be enough for convenient handling by the molybdate method. Small amounts of bismuth are more difficult to precipitate as molybdate, and the titration is not as reliable when only a few cubic centimeters of potassium permanganate are employed.

CONCLUSIONS.

The method proposed by Warwick and Kyle is founded on an old principle and the changes made by them make it worthless.

Bismuth is completely precipitated by hydrogen sulphide from a solution treated as follows: Tartaric acid is added to the acid solution; it is then made alkaline with caustic potash, a slight excess of potassium cyanide is added and the solution is precipitated with hydrogen sulphide. Under these conditions copper will remain in the solution. Small amounts of bismuth are quickly and easily separated from large amounts of copper in this way.

Bismuth is completely precipitated as bismuth ammonium molybdate by ammonium molybdate in a solution just acid with nitric acid. This precipitate can be washed with a 3 per cent. ammonium sulphate solution, and used for the determination of bismuth by dissolving in sulphuric acid, reducing the molybdenum and reoxidizing with potassium permanganate as in the method for phosphorus.

This separation and determination give a method equal in accuracy to the basic carbonate method, while the time necessary, especially when large amounts of copper are present, is very much less.

This work was carried out under the direction of Professor Edmund H. Miller, and it is with great pleasure that I take this opportunity of thanking him for the counsel and kind encouragement which he extended to me throughout the research.

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ON THE REDUCTION OF MOLYBDENUM BY ZINC AND THE RATIO OF BISMUTH TO MOLYBDENUM IN BISMUTH AMMONIUM MOLYBDATE.

BY EDMUND H. MILLER AND HENRY FRANK.

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NUMEROUS investigations have been made on the reduction of molybdenum by zinc in a reductor. W. A. Noyes[1] and Frohman came to the conclusion that the reduction corresponded to a salt of the oxide Mo_2O_3, provided that the air is displaced by carbon dioxide in the titrating flask. Blair[2] and Whitfield, however, although they followed Noyes and Frohman's conditions, could never attain a reduction equivalent to the oxide Mo_2O_3, but almost invariably obtained reduction equivalent to an oxide, $Mo_{24}O_{37}$. Other investigators have either confirmed the results of Blair and Whitfield or come to the conclusion that the reduction did not proceed even as far as $Mo_{24}O_{37}$, but to a point corresponding to an oxide of the formula $Mo_{12}O_{19}$. Drown,[3] however, by the use of 100-mesh zinc in a closed flask, has obtained a reduction corresponding to the oxide Mo_2O_3.

It was the object of this work to study the extent of the reduction produced in a reductor when the conditions, such as the length of the column of zinc, the acidity, the temperature and the atmosphere were varied, and to see whether the oxide Mo_2O_3 could be reached (Part I). And also, when the conditions for a definite degree of reduction were obtained, to apply these to the confirmation of the ratio of bismuth to molybdenum in the new bismuth

[1] This Journal, **16**, 553.
[2] *Ibid.*, **17**, 747.
[3] Blair's "Chemical Analysis of Iron," 4th edition, p. 99.

ammonium molybdate described by Riederer in the preceding article (Part II).

PART I.

About 6 liters of ammonium molybdate solution were made containing 10 grams of $(NH_4)_6Mo_7O_{24}.2H_2O$ per liter. This was standardized by precipitating as lead molybdate, giving the following values per cubic centimeter in grams of molybdic oxide, 0.008032 : 0.008034 : 0.008037 : 0.008026 : 0.008024; average, 0.008031.

Neither conversion of the sulphide to oxide nor evaporation of the solution with nitric acid gave concordant results, so, to obtain a check by another method, Smith's electrolytic method was followed exactly, which gave for two determinations 0.008020 and 0.008035 gram of molybdic oxide per cubic centimeter, thus confirming the accuracy of the lead molybdate determinations.

A sufficient quantity of potassium permanganate solution was prepared and standardized both against ferrous ammonium sulphate and oxalic acid. The value was 0.004546 gram of iron per cubic centimeter.

According to the reactions

$$5Mo_{12}O_{19} + 34KMnO_4 = 60MoO_3 + 17K_2O + 34MnO, \quad (1)$$

$$5Mo_{24}O_{37} + 70KMnO_4 = 120MoO_3 + 35K_2O + 70MnO, \quad (2)$$

$$5Mo_2O_3 + 6KMnO_4 = 10MoO_3 + 3K_2O + 6MnO, \quad (3)$$

the value of this permanganate solution in grams of MoO_3 is

0.004133. $12Mo = 34Fe$. $Mo_{12}O_{19}$ to MoO_3, (1)

0.004015. $12Mo = 35Fe$. $Mo_{24}O_{37}$ to MoO_3, (2)

0.003903. $12Mo = 36Fe$. Mo_2O_3 to MoO_3, (3)

using the atomic weights of 1903, Fe, 55.9 and Mo, 96.

Experiment I.—An ordinary reductor was used with a 10-inch column of unamalgamated zinc (20-30 mesh); the bulk of the solution was 200 cc.; the acidity, 10 cc. concentrated sulphuric acid; the temperature, 75° C. The molybdate solution was followed immediately by 100 cc. of hot water and titrated at once in the reductor flask. The permanganate required for the iron in the zinc was deducted throughout. The time required for the solution to pass through the reductor was two minutes in this case.

The results were:

Ammonium molybdate. cc.	$KMnO_4$. cc.	MoO_3. Gram.	Value of $KMnO_4$ per cc. in grams of MoO_3.
20	40.0	0.1606	0.004015
25	49.8	0.2007	0.004030
21	41.8	0.1687	0.004027

The results of this first experiment, though not very concordant, show an approximation to the value 0.004015 which corresponds to reduction equivalent to $Mo_{24}O_{37}$.

Experiment II.—Here and throughout the rest of the work a long glass tube, provided with a glass stop-cock, was used as a reductor. In this set of experiments, the length of the column of zinc was 15 inches; the time of passage 5-7 minutes; the temperature, 75° C.; the bulk of solution, 200 cc.; of wash water, 100 cc.; the acidity, 10 cc. of concentrated sulphuric acid.

The results were as follows:

Ammonium molybdate solution. cc.	$KMnO_4$. cc.	MoO_3. Gram.	Value of $KMnO_4$ in grams of MoO_3.
20	40.00	0.1606	0.004015
22	44.10	0.1767	0.004007
12	24.28	0.0964	0.003970
21	42.20	0.1687	0.003998
20	40.00	0.1606	0.004015
20	40.20	0.1606	0.003995
20	40.12	0.1606	0.004003
		Average,	0.0040004

With the longer time and the longer column of zinc, the results show a satisfactory agreement and that the reduction has proceeded slightly beyond $Mo_{24}O_{37}$. The factor for the MoO_3 standard calculated from these results is 0.88, the factor for phosphorus in the yellow precipitate 0.01579.

Similar experiments were made at a temperature of 25° C., with both a long and a short reductor, but the results were unreliable.

Experiment III. Reduction and Titration in an Atmosphere of Carbon Dioxide.—The apparatus consisted of a 500 cc. wide-mouthed bottle, fitted with a three-hole, rubber stopper. Through one hole the end of the reductor was passed, through the second the long tip of a burette, while the third was provided with a tube connecting with the suction. The procedure was as follows: The air in the reductor was first displaced by sucking a stream of carbon dioxide through it and then filled with air-free water to a height of 3 inches above the level of the zinc. Five grams of sodium bicarbonate were placed in the bottom of the bottle and then all the air replaced by carbon dioxide from a generator; then 5 cc.

of dilute sulphuric acid were poured in the bottle and the cork, containing the burette filled with permanganate and the reductor, fitted tight. The suction was turned on, and 100 cc. of hot, acidulated water (5 cc. of sulphuric acid in 100 cc.) passed through the reductor, followed immediately by the molybdate solution, and this in turn by 100 to 150 cc. of wash-water containing 3 cc. of sulphuric acid, taking care that the solution never went below the level of the zinc. When sufficient wash-water had passed through, the stop-cock of the reductor was turned off and the titration made at once. A blank was run and the iron in the zinc allowed for. The important conditions were: Time of passage, 7-10 minutes; temperature, 70°-75° C.; volume of molybdate solution, 200 cc.; acidity, 10 cc. concentrated sulphuric acid; length of column of zinc, 15 inches (not amalgamated). Results were:

Ammonium molybdate solution. cc.	$KMnO_4$. cc.	MoO_3. Gram.	Value of $KMnO_4$ in grams of MoO_3.
25	51.00	0.2007	0.003935
26	53.15	0.2088	0.003928
20	40.70	0.1606	0.003946
20	40.60	0.1606	0.003955
21	42.80	0.1687	0.003941
25	50.90	0.2007	0.003943
19	38.80	0.1526	0.003933
20	40.70	0.1606	0.003946
20	40.65	0.1606	0.003951
25	50.90	0.2007	0.003943
		Average,	0.003942

As the theoretical strength of the permanganate would be 0.003903 if the reduction were to Mo_2O_3, it is evident that this has not been attained, but that the reduction is to a point a little below midway between $Mo_{24}O_{37}$ and Mo_2O_3.

Experiment IV. Another Attempt to Reach Mo_2O_3.—The solution was first passed through a short reductor (Experiment I) and then was treated as in Experiment III, using an atmosphere of carbon dioxide, etc. Results were:

Ammonium molybdate. cc.	$KMnO_4$. cc.	MoO_3. Gram.	Value of 1 cc. $KMnO_4$ in grams MoO_3.
25	51.10	0.2007	0.003927
26	53.18	0.2088	0.003926
20	40.93	0.1606	0.003921
21	42.95	0.1687	0.003951
19	38.85	0.1526	0.003951
18	36.76	0.1446	0.003933
23	46.97	0.1847	0.003932
		Average,	0.003933

The volume at the first reduction was 100 cc., containing 5 cc.

concentrated sulphuric acid after passing the first reductor; it was made up to 200 cc. after 5 cc. more of sulphuric acid had been added. The time of passage was eight to ten minutes. The results do not differ sufficiently from those of Experiment III to deserve comment.

In order to test the rapidity of reoxidation by air, two more portions, each containing 0.1606 gram of molybdenum trioxide, were reduced, as just described, in an atmosphere of carbon dioxide, then before titration a blast of air was forced through, in one case for three, in the other for four minutes.

A. Blast for 3 minutes required 39.08 cc. $KMnO_4$ or 1 cc. = 0.004109.
B. " " 4 " " 38.50 " " " 1 " = 0.004171.

Had there been no reoxidation, 40.83 cc. of $KMnO_4$ would have been required. The reoxidation to $Mo_{12}O_{19}$, equivalent to 0.004133, would have been accomplished in three and one-half minutes under those conditions.

Experiment V.—Identical with II except that amalgamated zinc was used. Results were:

Ammonium molybdate solution. cc.	$KMnO_4$. cc.	MoO_3. Gram.	Value of $KMnO_4$ in grams MoO_3.
20	39.9	0.1606	0.004027
25	49.9	0.2007	0.004022
21	42.0	0.1687	0.004016
20	40.0	0.1606	0.004015
26	51.9	0.2088	0.004023
23	46.0	0.1847	0.004015
		Average,	0.0040196

The reduction does not proceed quite as far as with the unamalgamated zinc, although the difference is hardly more than the experimental error. The average result is very close to reduction to $Mo_{24}O_{37}$, while the three lowest and most concordant results agree exactly with the calculated value for that oxide—0.004015.

Experiment VI.—This is a repetition of IV, except that amalgamated zinc was used. The results were:

Ammonium molybdate. cc.	$KMnO_4$. cc.	MoO_3. Gram.	Value of $KMnO_4$ in grams of MoO_3.
25	51.0	0.2007	0.003935
25	50.8	0.2007	0.003951
29	59.1	0.2329	0.003941
26	53.0	0.2088	0.003940
24	48.8	0.1927	0.003949
21	42.7	0.1687	0.003951
20	40.6	0.1606	0.003955
20	40.7	0.1606	0.003946
21	42.6	0.1687	0.003960
		Average,	0.0039475

This is practically the same result as with the unamalgamated zinc, though here, as in the preceding experiment, there is a tendency for the amalgamated zinc to give a slightly less complete reduction.

Experiment VII.—Reduction with Zinc Foil in a Flask.—Twenty cc. of the standard ammonium molybdate solution were diluted to 100 cc. and placed in a flask with four pieces of thin sheet zinc, 1 inch square, and 15 cc. of sulphuric acid, and boiled for twenty minutes. The solution became deep green in color, but on dilution to 300 cc. with *cold* water it changed to port-wine color. The results were 39.1 cc. and 38.9 cc. of the permanganate solution, so that the reduction was very nearly equivalent to $Mo_{12}O_{19}$.

Average result, 1 cc. $KMnO_4$ = 0.004118.
Theory for $Mo_{12}O_{19}$, 1 cc. $KMnO_4$ = 0.004133.

The same experiments were repeated, except that the solution was boiled for half an hour and then diluted to 300 cc. with *hot,* air-free water. The solutions retained their deep green color and required 40 cc. and 40.15 cc. of permanganate for their reoxidation. These results are equivalent to 0.004015 gram MoO_3 and 0.004000 gram MoO_3 per cubic centimeter of permanganate, agreeing with reduction to $Mo_{24}O_{37}$, as obtained in Experiment II.

Magnesium and aluminum were also tried, but without satisfactory results.

Experiment VIII.—Blair's[1] conditions for the reduction of molybdenum were followed exactly. Twenty cc. of the ammonium molybdate solution was diluted to 150 cc., 20 cc. of sulphuric acid added and finally 5 grams of pulverized zinc. The solution was heated in order to start the reaction and then the stopper, containing a tube bent twice at right angles, was inserted. The other end of the tube dipped into a saturated solution of sodium bicarbonate. After complete solution of the zinc, which usually required about an hour, the green solution was immediately titrated with permanganate. Results were as follows:

$KMnO_4$. cc.	MoO_3. Gram.	Value of $KMnO_4$ in grams of MoO_3.
41.5	0.1606	0.003870
41.3	0.1606	0.003888
41.6	0.1606	0.003861
41.4	0.1606	0.003879
	Average,	0.0038745

[1] "Chemical Analysis of Iron," 3rd edition.

The calculated value for reduction to Mo_2O_3 is 0.003903. The results show that this reduction is fully obtained, but the method is not as satisfactory as the reductor.

CONCLUSIONS.

In general, we have confirmed Blair's statements in all respects and have not succeeded in obtaining reduction to Mo_2O_3 in a reductor. Our work has emphasized the importance of absolute uniformity in the conditions for both reduction and titration with with those used when the factor was obtained, as stated by W. A. Noyes. There is no definite stopping point at $Mo_{24}O_{37}$, though the reduction under the usual conditions proceeds very close to this point.

When the reduction is accomplished under the following conditions: Length of column of 20-30 mesh zinc, 15 inches; time of passage, about 6 minutes; temperature, 70°-75° C.; volume, 200 cc.; acidity, 10 cc. of concentrated sulphuric acid; and the titration is made in the reductor flask without dilution or delay, but using no atmosphere of carbon dioxide, the factors are: For unamalgamated zinc, iron standard of permanganate times 0.88 gives MoO_3 standard; times 0.01579 gives phosphorus standard; when the "yellow precipitate" is titrated. For amalgamated zinc these factors are 0.8842 and 0.01586. The factors based on reduction to $Mo_{24}O_{37}$ are 0.8832 and 0.01584, using the atomic weights of 1903.

PART II.

Bismuth ammonium molybdate was prepared as follows: Ten cc. of the standard bismuth nitrate solution (described in the preceding article) were run into a beaker and 100 cc. of the ordinary acid ammonium molybdate reagent were added, the solution diluted to about 200 cc. and heated on an asbestos disk by a Bunsen burner. While the heating was in progress, ammonia (sp. gr. 0.96) was run in from a burette and the solution stirred vigorously. The addition of ammonia caused the formation of a precipitate and gave a yellow color to the solution which, as the neutral point was approached, disappeared, and a bluish tint was noticeable. This was used as an indication that sufficient ammonia had been added. The solution must be very hot, but not boiling, and the precipitate pure white. It was washed free from molybdenum by a 3 per cent. solution of ammonium sulphate, then into a

clean beaker with hot water. Ten cc. of sulphuric acid were added, and the solution was reduced and titrated under conditions of Experiment II. Assuming that there are present in the precipitate 2 molecules of MoO_3 for each atom of bismuth, the strength of the permanganate solution is 0.002896 gram bismuth per cubic centimeter. The results of three determinations were:

$KMnO_4$. cc.	Bi taken.	Bi found.	Calculated BiMo ratio.
39.60	0.1155	0.1147	1 : 1.986
39.75	0.1155	0.1151	1 : 1.993
39.70	0.1155	0.1150	1 : 1.991

The reduction and titration were then made according to the conditions of Experiment III; the bismuth value of the permanganate becomes 1 cc. = 0.002854. The results were:

$KMnO_4$. cc.	Bi taken.	Bi found.	Calculated BiMo ratio.
40.40	0.1155	0.1153	1 : 1.997
40.35	0.1155	0.11515	1 : 1.994

As methyl orange was not found a satisfactory indicator in the precipitation of bismuth by this method, others were tried and congo red was adopted as the most convenient. We next carried out the precipitation as follows: To the solution containing bismuth nitrate and 5 per cent. of free nitric acid, a decided excess of the ordinary molybdate reagent was added; there should be no precipitate produced at this point. A few drops of congo red were added and then very dilute ammonia slowly from a burette, with stirring; in a short time a white precipitate began to appear. We continued to add ammonia (in the cold) till the indicator became pink; next a few drops of dilute nitric acid were added so that the color was lilac (just neutral). The solution was warmed on a thick asbestos pad, but not to boiling. The precipitate collected and filtered well. It looked like silver chloride and was extremely easy to wash. The indicator was decomposed on heating and separated out as a pink lake, which adhered to the filter-paper.

Under the conditions given, the precipitation is absolutely complete, but if too much nitric acid is added, so that the indicator is turned back to a decided blue color, the precipitate does not collect or filter as well and the filtrate may contain traces of bismuth.

Two precipitates made in this way were analyzed as follows: After decomposition by ammonium sulphide, the bismuth sulphide was dissolved in nitric acid and weighed as oxide. The molybdenum was precipitated from the ammonium sulphide filtrate by

making slightly acid with hydrochloric acid and allowing to stand for several hours. The sulphide was dissolved in aqua regia, evaporated to small volume, neutralized with ammonia and then precipitated as lead molybdate. The results were:

No. 1. Weight $PbMoO_4$ 0.7558 gram = Mo 0.1977 gram.
" Bi_2O_3 0.2456 gram = Bi 0.2202 gram.
Atomic ratio Bi : Mo : : 1 : 1.95.
No. 2. Weight $PbMoO_4$ 0.6172 gram Mo = 0.1615 gram.
" Bi_2O_3 0.1951 gram Bi = 0.1747 gram.
Atomic ratio Bi : Mo : : 1 : 2.007.

Two portions of 10 cc. each of the standard bismuth solution were precipitated and the precipitates analyzed for ammonia. After deducting the relatively large amount present as ammonium sulphate, 0.0588 gram,[1] from the total ammonia, 0.06722 gram, the ammonia (NH_3) in combination with 0.1155 gram of bismuth was 0.0084 gram in one case, and 0.0598—0.05182 or 0.00806 gram in the other. These values give Bi : NH_3 ratios of 1 : 0.9- and 1 : 0.85 respectively or 4.24 and 4.06 per cent. $(NH_4)_2O$ compared with the theory for $BiNH_4(MoO_4)_2$, 4.76 per cent. Although these precipitates were sucked dry on a Büchner funnel to remove as much as possible of the excess of ammonium sulphate,[2] the relatively large quantity of ammonium as sulphate renders the accurate determination of that existing in combination with the bismuth a matter of difficulty.

The following experiments were made to see whether there was any variation in the composition of the precipitate when formed according to the three methods given. The results are in grams of bismuth, obtained by the titration method already fully described.

A. Riederer's conditions; methyl orange indicator; solution just acid with nitric acid; bismuth taken, 0.1280; found, 0.1278.

B. Congo red as indicator; solution neutral; bismuth taken, 0.1280; found, 0.1285 and 0.1288. (These slightly high results may be due to the carrying down of molybdenum by the indicator to form a lake.)

C. No indicator; solution made slightly alkaline; bismuth taken, 0.1280; found, 0.1274 and 0.1277.

CONCLUSION.

The peculiar properties of this precipitate,—that it cannot be

[1] Calculated from the SO_4 determined as $BaSO_4$.
[2] As suggested by Professor W. A. Noyes.

washed with water or dried without decomposition, make the determination of its composition a matter of extraordinary difficulty, as everything must be found by ratios, and the ammonia determination is complicated by the ammonium sulphate present. But from the preceding determinations and others by other workers, there seems to be no doubt that the ratio of bismuth to molybdenum is as one is to two and that if the formula is not $BiNH_4(MoO_4)_2$, the variation is extremely slight and not such as to prevent the use of this precipitate for the volumetric determination of bismuth.

QUANTITATIVE LABORATORY,
June 20, 1903.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.]

THE CONSTITUTION OF POTASSIUM RUTHENIUM NITROSOCHLORIDE IN AQUEOUS SOLUTION.

BY S. C. LIND.

Received June 15, 1903.

THIS salt is the one which led Claus in 1845 to identify ruthenium as a new metallic element. He supposed it, however, to have the formula K_2RuCl_6, and, therefore, to belong to the well-known class of salts represented by K_2PtCl_6. In 1888, A. Joly[1] showed that this is not the case, but that the compound is a mononitroso salt of the formula K_2RuCl_5NO. The properties of this salt and analyses of it by several authors are presented in Freeny's "Encyclopedie Chimique."[2] J. L. Howe[3] has confirmed this interesting discovery and has described the salt very fully, and given new analytical data in regard to it.

The properties presented by this salt, its rather unique formula, and also its relation to several other analogous ruthenium salts, have made a study of its constitution in aqueous solution of interest. Such an investigation was undertaken at the suggestion of Dr. Jas. L. Howe, to whom the author is indebted for the salt used in the following measurements. His analyses were made on this same sample; they will be found in his article referred to above. The author also desires to acknowledge his indebtedness

[1] *Compt. Rend.*, **107**, 994 (1888).
[2] "Encyclopedie Chimique," III, **17**, I, 179-181.
[3] This Journal, **16**, 388 (1894).

to Dr. Arthur A. Noyes for his supervision of, and assistance in, this investigation.

The following determinations have been made. First, the electrical conductivity of the salt at 22°, at various concentrations from $^1/_{20}$ to $^1/_{2560}$ normal; second, the lowering produced by the salt in the freezing-point of water; third, the direction of the migration of the ruthenium during electrolysis.

I. CONDUCTIVITY MEASUREMENTS.

The apparatus used was the ordinary slide wire-bridge arrangement of Kohlrausch. The temperature employed was 22° (corrected), kept constant within 0.1° by means of a thermostat. The amount of salt required to make 100 cc. of an N/20 solution (that is, one containing $^1/_{40}$ K_2RuCl_5NO per liter) was dissolved in a weighed amount of water. This was used as a stock solution for making the more dilute solutions.

The salt was found to be perfectly stable in water solution at all the various concentrations, the conductivity of the solutions not changing at all in two weeks.

In the following table, the conductivity values obtained at the various dilutions, are given, expressed in reciprocal ohms. For comparison are also given the corresponding values for potassium platinic chloride at the same dilutions. These values were obtained from Walden's measurements at 25° by applying a temperature correction of 2.2 per cent. per degree, to the values for the different dilutions, obtained by interpolations from plots. The change from the Siemen's unit to the reciprocal ohm was effected by dividing each value by 1.063.

The specific conductivity of the water used in dissolving the salt and making the dilutions was 1.4×10^{-6} reciprocal ohms. This was subtracted in each case from the specific conductivity of the solution before calculating the equivalent conductivity.

TABLE I.—CONDUCTIVITY VALUES AT 22°.

Liters per equivalent.	Equivalent K_2RuCl_5NO.	Conductivity. K_2PtCl_6.
20	99.8	....
40	106.4	96.6
80	110.3	101.5
160	115.4	105.4
320	118.5	108.5
640	121.9	111.1
1280	126.0	113.4
2560	127.5	....

II. FREEZING-POINT LOWERING.

The method employed was the usual one described by Raoult. A correction was applied to the observed lowering for the increased concentration of the solution by the ice separated from it. This correction was calculated from the heat of fusion and the supercooling of the solution, which was 1.5 to 3.5°.

TABLE II.—FREEZING-POINT LOWERING.

	Weight of solvent. Grams.	Weight of salt. Gram.	Liters per mol.	Observed lowering.	Corrected lowering.	Molecular lowering.	van't Hoff's coefficient *i*.	Percentage dissociation.
I.	20	0.4084	18.9	0.261°	0.251°	47.59	2.56	78.0
II.	20	0.4001	19.9	0.251°	0.242°	46.87	2.52	76.0
III.	20	0.2240	34.6	0.153°	0.148°	51.17	2.75	87.5
IV.	20	0.1052	73.4	0.071°	0.069°	50.59	2.72	86.0

By making a plot, using the conductivity values as abscissas and the cube roots of the corresponding concentrations as ordinates, a straight line is obtained. If this line be continued to zero concentration, a value is obtained for conductivity at infinite dilution, which in this case is found to be 133.5. This maximum conductivity of the salt represents its complete dissociation; therefore, from the ratio $\frac{\Lambda_{20}}{\Lambda_{\infty}}$, the percentage dissociation of the N/20 solution is found to be 74.7 per cent., slightly lower than the value found by the freezing-point method. From the above table, it appears that the salt is partially dissociated into *three ions,* as would be expected if we assign to it the formula $2K/RuCl_5NO$.

III. MIGRATION OF THE RUTHENIUM ION.

The solutions of this salt have a very characteristic violet-red color, which is due to the ruthenium ion. This seemed to offer a good opportunity of investigating the direction of motion of the colored ions under the influence of a direct electric current.

The form of apparatus used was suggested to the author by Mr. A. C. Melcher, and is so simple and so well adapted to experiments of this kind, that it may be briefly described.

A 2 per cent. solution of agar jelly in water was prepared, and to it was added a quantity of potassium chloride, sufficient to make an N/20 solution. Two 3-inch U-tubes were exactly filled with the jelly solution, which was then congealed by immersion in an

ice-bath. An approximately N/20 solution of the potassium ruthenium nitrosochloride was prepared in a small beaker. One arm of each of the two inverted U-tubes was dipped into this solution to a depth of about 6 mm. The other arm of one of the tubes was immersed in a beaker containing a hydrochloric acid solution, and that of the other tube into a similar beaker containing a caustic potash solution. Into these two beakers were introduced platinum electrodes, and a direct current was passed so that the *anode* was in the beaker containing the *acid* solution, and the cathode in that containing the alkaline solution. The purpose of these two solutions was to neutralize the products of electrolysis set free at the electrodes. Their concentration is immaterial.

A 110-volt current was then passed through the system. After its passage for a few minutes, a pink layer appeared above the surface of the solution, in the arm on the anode side, and moved steadily toward that electrode. This extension of the color zone continued regularly, with a well-defined and perfectly level boundary, at a rate of about 5 cm. per hour. On the other hand, in the cathode arm, not a trace of color appeared either above or below the surface of the solution.

This decisive result shows that the ruthenium is a constituent of the negative ion, and that there are no positive ions containing ruthenium in the solution. This consideration, together with the facts already shown in regard to the number of ions into which the salt dissociates, shows its structure to be $2K^+/RuCl_5NO^{--}$.

SUMMARY.

By way of summary, the following points in regard to the structure and properties of this salt may be mentioned, as having been established by the foregoing experiments.

(1) It is perfectly stable in aqueous solution, as is shown by the fact that its conductivity does not change at all in two weeks.

(2) It has a molecular conductivity very close to that of the analogous salt, potassium platinic chloride.

(3) The salt is partially dissociated into three ions as shown by its effect on the freezing-point of water. The value of van't Hoff's coëfficient *i*, is 2.52-2.72 in $^1/_{20}$-$^1/_{70}$ molar solution.

(4) The degree of dissociation of the salt, derived from the freezing-point lowering, agrees well with that obtained by conductivity measurements; it also agrees with the value for potassium platinic chloride.

(5) The direction of migration of the colored ions shows that the ruthenium is present in the negative ion, and in that alone.

(6) It will be seen from Table I, that the values for the ruthenium salt are uniformly about 10 per cent. greater than those for the platinum salt. It is evident, therefore, that the dissociation relations are entirely similar.

THE ACTION OF FUMING SULPHURIC ACID UPON ISOAMYL CHLORIDE.

By R. A. Worstall.

Received June 24, 1903.

Some years ago, while the author was engaged upon an investigation of aliphatic sulphonic acids, some preliminary work was done upon the products of the reaction between isoamyl chloride and fuming sulphuric acid. It was the author's intention to make an extended study of the action of sulphuric acid of various degrees of concentration upon different alkyl haloids, but owing to pressure of other work this investigation was dropped, and neither the opportunity nor the facilities have since been available for completing this work. As it does not seem probable that opportunity will be afforded for any further work along this line, it may not be amiss to publish the results of the investigation so far as it was carried.

The following is a brief résumé of the literature upon the subject of the reactions between sulphuric acid and alkyl haloids. Williamson,[1] by the action of sulphuric anhydride upon ethyl chloride, obtained chlorethyl sulphuric acid, a heavy oil, decomposed by water into hydrochloric acid, sulphuric acid and ethyl sulphuric acid. Methyl chloride gave a similar result. By the action of chlorsulphuric acid upon the alcohols, the same compounds resulted.

Oppenheim[2] states that amyl chloride with concentrated sulphuric acid gave amyl sulphuric acid, and that all alkyl chlorides, by similar treatment, lose hydrochloric acid and form alkyl sulphuric acids. The same author,[3] by acting upon ethylene chloride and its homologues with concentrated sulphuric acid in sealed

[1] *J. prakt. Chem.*, **73**, 73.
[2] *Am. Chem. J.*, **6**, 353.
[3] *Ber. d. chem. Ges.*, **2**, 212.

tubes at 130° C., obtained decomposition into carbon, sulphur dioxide and hydrochloric acid. No action was apparent at ordinary temperatures.

Wroblewsky[1] found that sulphuric anhydride with ethylene bromide separated bromine and hydrobromic acid and gave brom-

ethyl sulphonic acid, $C_2H_4\begin{matrix}Br\\SO_2OH\end{matrix}$, from which the barium salt was obtained. Ethyl iodide with sulphuric anhydride gave ethyl sulphonic acid.

Purgold,[2] by the action of sulphuric anhydride on ethyl chloride, obtained chlorethyl sulphate, chlorethyl sulphonic acid, and oxyethyl sulphonchloride. Armstrong[3] studied the action of sulphuric anhydride on chloroform, carbon tetrachloride and carbon hexachloride, obtaining chlorcarbonic and chlorsulphuric acids.

For the sulphonation of amyl chloride, 30 grams of isoamyl chloride were added gradually to 60 grams fuming sulphuric acid, and the mixture kept cool. Heat was generated with slight evolution of sulphur dioxide. When the reaction was complete, the solution was poured into water and the milky liquid extracted three times with ether. The acid solution was neutralized with barium carbonate and filtered. The filtrate was evaporated to dryness. A white salt was left, which was very deliquescent and which darkened somewhat at the temperature of the steam-bath. The salt was extracted with hot 90 per cent. alcohol and filtered. A large excess of ether in the filtrate precipitated a flocculent, white barium salt, the precipitation not being complete. This salt was analyzed after washing with ether and drying, and found to be impure, containing barium chloride.

The sulphonation was repeated, using 50 grams of isoamyl chloride and 200 grams of fuming sulphuric acid. The reaction mixture was poured into water and this solution extracted three times with ether. The ether solution was washed and evaporated. The residue of 12 grams was a red, oily liquid of a disagreeable odor, and was not further investigated. The water solution was neutralized with barium carbonate, filtered, the filtrate evaporated to a small volume, and an equal volume of 90 per cent. alcohol added. This solution was then evaporated to half its volume and

[1] *Ztschr. Chem.* (1868), p. 563.
[2] *Ber. d. chem. Ges.*, **6**, 502.
[3] *J. prakt. Chem.* [2], 244.

allowed to stand. On cooling, beautiful, needle-like crystals, nearly an inch long, separated. These were removed and dried, first between filter-paper, then by standing in a desiccator over sulphuric acid. After standing in the desiccator for a day, the crystals began to whiten and crumble, showing that they were losing water of crystallization. The salt was, therefore, recrystallized from 60 per cent. alcohol and dried between filter-paper. In all, about 40 grams of this salt were obtained.

Analysis of the crystallized salt gave the following results: For moisture, 1.1218 grams lost 0.0824 gram at 100°, equivalent to 7.34 per cent. H_2O. $\left(C_5H_{10}<\begin{matrix}OH\\SO_3\end{matrix}\right)_2Ba.2H_2O$ should contain 7.10 per cent. H_2O.

The salt dried at 100° gave the following figures:

	Calculated for $\left(C_5H_{10}<\begin{matrix}OH\\SO_3\end{matrix}\right)_2Ba.$	Found.
Barium	29.09	29.05
Sulphur	13.58	13.98

Even the last crystals from the mother-liquor gave no test for chlorine, proving that no chlorsulphonic acid was formed. $\left(C_5H_{10}<\begin{matrix}OH\\SO_3\end{matrix}\right)_2Ba$ and $\left(SO_2<\begin{matrix}OC_5H_{11}\\O\end{matrix}\right)_2Ba$ are isomers. The latter is known to crystallize with $2H_2O$. The former has been reported anhydrous. A concentrated solution of the salt was acidified and boiled with dilute hydrochloric acid. It developed no pink color, no precipitate and no odor of fusel oil. The lead salt was prepared, decomposed by hydrogen sulphide and the free acid boiled. It gave, after long boiling, only a faint test for sulphuric acid. Some isoamyl sulphate was prepared from isoamyl alcohol and concentrated sulphuric acid, and the barium salt formed. The aqueous solution of the latter, even when dilute, when acidified with hydrochloric acid and boiled, gave a pink color, the odor of fusel oil, and a precipitate of barium sulphate. Hence there seemed no doubt that the compound described was barium oxyisoamyl sulphonate, and that it crystallizes with two molecules of water. Mewes[1] has shown that ethyl sulphate, by the action of fuming sulphuric acid, is converted into oxyethyl sulphonic acid. Hence it is possible that the first product of the reaction between isoamyl chloride and fuming sulphuric acid is isoamyl sulphate, and that this, by further action, is converted into the

[1] *Ann. Chem.* (Liebig), **143**, 196.

oxysulphonic acid. There is, however, no experimental evidence to prove this.

CHICAGO VARNISH CO.,
CHICAGO, June, 1903.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 86.]

3,5-BIBROM-2-AMINOBENZOIC ACID: ITS NITRILE AND THE SYNTHESIS OF QUINAZOLINES FROM THE LATTER.[1]

BY MARSTON TAYLOR BOGERT AND WILLIAM FLOWERS HAND.

Received July 25, 1903.

ATTEMPTS to brominate nitrites have usually resulted unsuccessfully, and the bromination of anthranilic acid has given only tribromaniline. By the use of the calculated amount of nascent bromine, however, we have succeeded in introducing two atoms of bromine, not only into the molecule of anthranilic acid, but also into that of its nitrile, the brominating agent being an aqueous solution of potassium bromide and bromate, in the proportion of five molecules of the former to one of the latter, which, upon acidifying, liberates exactly 3 molecules of bromine, according to the following equation:

$$5KBr + KBrO_3 + 6HCl = 3Br_2 + 6KCl + 3H_2O.$$

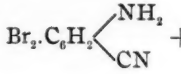
A standard solution of bromide and bromate, 1 cc. of which, upon being acidified, liberated 0.0800 gram of bromine, gave very satisfactory results.

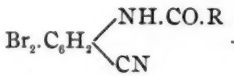
With both anthranilic acid and its nitrile, the bromine entered in the ortho-para positions with reference to the amino group, giving 3,5-bibrom-2-aminobenzoic acid and its nitrile, from which, by elimination of the amino group, 3,5-bibrombenzoic acid and its nitrile were obtained. This elimination of the amino group was accomplished with the greatest difficulty, the yield of the bibrombenzoic compound being small.

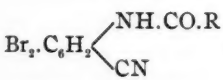
The bibromanthranilic nitrile we have converted into quinazolines and thioquinazolines by the use of the methods previously reported by us,[2] the equations being as follows:

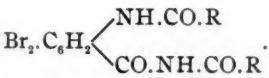
[1] Read at the Cleveland meeting of the American Chemical Society, June 30, 1903.

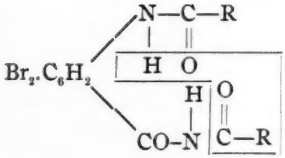
[2] This Journal, **24**, 1031; **25**, 372.

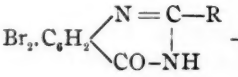
I. 

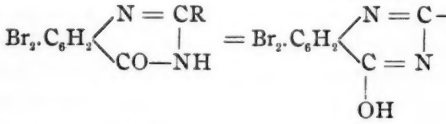


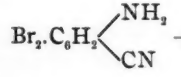


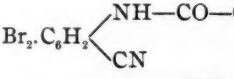


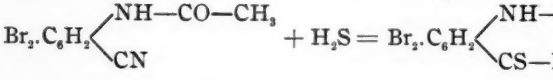


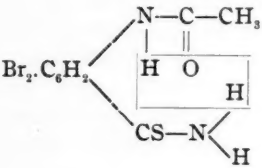


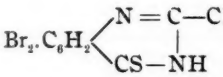


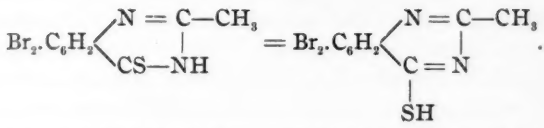
II. 











By these reactions, 6,8-bibrom-2-alkyl-4-ketodihydroquinazolines the corresponding methyl thioquinazoline, and certain of their derivatives have been prepared.

EXPERIMENTAL PART.

BROMINATION OF ANTHRANILIC NITRILE. 3,5-BIBROM-2-AMINOBENZONITRILE.

The anthranilic nitrile used in these experiments was prepared by the method described in our previous paper.[1]

Bromination in Carbon Tetrachloride, Benzene, or Aqueous Solution.—On adding a carbon tetrachloride solution of bromine to a similar one of anthranilic nitrile, a white, amorphous precipitate immediately separates, which melts at (roughly) about 195°-200°. By a single crystallization of this product from alcohol, colorless needles of considerable length are obtained, melting quite sharply at 95.5° (corr.). Bromination in benzene or in aqueous solutions appears to yield similar results. This product has not as yet been further investigated.

Bromination with Hypobromite, and with Nascent Bromine.—Three grams of anthranilic nitrile were dissolved in dilute alcohol, dilute hydrochloric acid added, and then sufficient alkaline potassium hypobromite solution gradually stirred in to form a bibrom-derivative. Small, white, feathery needles separated, which melted sharply at 156°-156.5° (corr.) after several recrystallizations from 95 per cent. alcohol. A portion was sublimed, and the sublimate showed exactly the same melting-point.

	Found.	Calculated for $C_7H_4N_2Br_2$.
Nitrogen	10.38	10.15
Bromine	57.73	58.00

A solution of bromide and bromate of potassium was prepared as already described. The anthranilic nitrile was dissolved in about ten parts of strong alcohol, acidified with hydrochloric acid,

[1] This Journal, **24**, 1035.

and the calculated amount of the brominating solution poured in. At first we used a large excess of dilute hydrochloric acid and cooled with ice, but later found both these precautions unnecessary. The brownish substitution product separates at once. It is washed thoroughly, dissolved in the smallest possible amount of 95 per cent. alcohol on the water-bath, hot water added until the cloud formed redissolves but slowly, and the solution is then allowed to cool. The bibromanthranilic nitrile separates very completely, in needles, the yield being nearly theoretical, and the product quite pure. A single recrystallization will usually remove the last traces of color from the crystals, the substance being identical in all respects with that obtained by the action of the hypobromite.

This bibrom nitrile forms no salt when hydrochloric acid gas is passed through its dry ethereal solution; nor is it acetylated by long boiling with acetic anhydride, the amino group remaining unaffected. To determine the position of the bromine atoms in the molecule, the saponification of the nitrile was undertaken.

SAPONIFICATION OF 3,5-BIBROM-2-AMINOBENZONITRILE.

Potassium Hydroxide.—The bibrom nitrile was boiled for some time with caustic potash of various strengths, with but little effect. A small amount was dissolved, and a few white needles separated on cooling. Very strong alkali appeared not to dissolve it at all, while fusion with potassium hydroxide gave only a yellow decomposition product.

Hydrochloric Acid.—The nitrile was unchanged by several hours' boiling with concentrated hydrochloric acid. When they were heated together in sealed tubes at 180° for several hours, partial saponification was secured, accompanied by some decomposition.

Sulphuric Acid.—Concentrated sulphuric acid charred the nitrile, but dissolved it completely on gentle warming. Acid of 75 per cent. to 85 per cent. strength gave a fairly good saponification, but the product was always brown, even after solution in caustic soda and reprecipitation with hydrochloric acid. In a sealed tube at 180°, however, 80 per cent. sulphuric acid gave a satisfactory saponification. Above 185°, rapid decomposition sets in. It is advisable to use as short a sealed tube as possible and to turn the same in the furnace from time to time, as the nitrile sublimes out of the sulphuric acid into the upper end of the tube and is thus liable to escape complete saponification. The contents

of the tube are poured into water, and the precipitate filtered out, washed and crystallized from alcohol, when white needles are obtained melting at 235.5°-236° (corr.). A portion sublimed showed exactly the same melting-point.

3,5-BIBROM-2-AMINOBENZOIC ACID.

The melting-point of the acid obtained by us, by saponification of the bibromanthranilic nitrile, does not coincide with that of any of the bibromanthranilic acids so far reported.

Hübner[1] gives the melting-point of the 3,5-bibrom-2-aminobenzoic acid as 225°, and exactly the same figure (225°) for the melting-point of the 3,4-bibrom-2-aminobenzoic acid, while Dorsch[2] found the melting-point of the 3,4-bibrom acid to be 226°-228°, and states that his acid is identical with that of Smith.[3]

We, therefore, decided to attempt the bromination of anthranilic acid itself in the same manner as its nitrile, in the hope of obtaining the same bibromanthranilic acid, and in this we were quite successful.

The anthranilic acid was dissolved in a very large volume of dilute hydrochloric acid and the bromide-bromate solution stirred in. The mixture turns blue and a precipitate slowly separates. After standing for half an hour, the precipitate is filtered out, washed thoroughly to remove unchanged anthranilic acid, etc., and then separated from any tribromaniline by solution in cold, dilute caustic soda and reprecipitation with hydrochloric acid.

By using rather less than the calculated amount of the brominating solution, very little tribromaniline is formed; any excess of bromine, however, above 2 molecules, increases the yield of tribromaniline and correspondingly diminishes that of the bibromanthranilic acid. With 3 molecules of bromine to 1 of anthranilic acid, only a trace of the bibromanthranilic acid was found, the product being nearly pure tribromaniline.

The precipitated bibromanthranilic acid is washed and treated with boneblack. The light amber solution thus obtained, on cooling, separates small needles nearly white. These needles are suspended in boiling water, baryta water is added to alkaline reaction, and the excess of baryta then removed by saturating the boiling solution with carbon dioxide. The barium carbonate and

[1] *Ann. Chem.* (Liebig), **222**, 175.
[2] *J. prakt. Chem.* (2), **33**, 36.
[3] *Ber. d. chem. Ges.*, **10**, 1706.

a small amount of material insoluble in baryta water are filtered out, and the filtrate evaporated to crystals. On cooling, the barium salt of the bibromanthranilic acid separates in small, white prisms, which are recrystallized from water, and then decomposed by hydrochloric acid. The bibrom acid thus liberated is crystallized from benzene and from alcohol, then appearing in needles of a faint yellowish cast, melting at 235°-235.5° (corr.), and identical in other respects with the acid obtained by the saponification of the bibromanthranilic nitrile. Both the acid and its barium salt are rather troublesome to purify, their solutions rapidly darkening when heated, and this may account for the low melting-point reported by Hübner.[1] Well-formed crystals can be obtained only by very slow cooling.

The pure 3,5-bibrom-2-aminobenzoic acid, as thus prepared, is easily soluble in alcohol (absolute), ether or acetone; moderately, in 95 per cent. alcohol, boiling benzene, or boiling toluene, but only sparingly in the latter two when cold; insoluble in ligroin; almost insoluble in water, cold or hot. It is decomposed, with loss of bromine, when gently heated with slaked lime. Heated alone in a sealed tube, at 260°-270° it decomposes with liberation of hydrobromic acid. By elimination of its amino-group, 3,5-bibrombenzoic acid is formed. By the action of dry hydrochloric acid gas upon its dry ethereal solution, the hydrochloride separates as a white powder, which, when washed with dry ether and dried, gives off hydrochloric acid very rapidly.

SALTS OF 3,5-BIBROM-2-AMINOBENZOIC ACID.

Alkaline Salts.—By evaporating concentrated aqueous solutions of the sodium or potassium salts over sulphuric acid *in vacuo*, these salts separate in needles of considerable length. On account of their great solubility in both water and alcohol, it is very difficult to purify them.

Barium Salt.—The preparation of this salt we have already outlined. It crystallizes in small needles, moderately soluble in boiling water, but only sparingly soluble in cold. The crystals carry 3.5 molecules of water, of which 1.5 molecules are removed by drying over sulphuric acid *in vacuo*. According to Hübner[1] the crystals contain $4H_2O$.

Some of the crystals, dried five hours at 100°, lost 7.89 per

[1] *Loc. cit.*

cent. in weight; $(C_6H_2Br_2(NH_2)COO)_2Ba.3\frac{1}{2}H_2O$ contains 7.99 per cent. water. A determination of the water in the crystals dried over sulphuric acid, *in vacuo,* gave 4.78 per cent. and 5.05 per cent.; $(C_6H_2Br_2(NH_2)COO)_2Ba.2H_2O$ contains 4.73 per cent. H_2O.

This latter product, containing $2H_2O$, was further analyzed for barium and nitrogen, with the following results:

	Found.		Calculated for $(C_6H_2Br_2(NH_2)COO)_2Ba.2H_2O$.
Barium	17.76	17.83	18.00
Nitrogen	4.90		4.74

When heated in an open tube, this barium salt takes fire and burns. By careful manipulation, however, a sublimate was obtained, melting at 74°-75° (corr.), which has not been further examined.

ELIMINATION OF THE AMINO-GROUP FROM 3,5-BIBROM-2-AMINOBENZONITRILE.

The bibrom nitrile was suspended in water, hydrochloric acid added, and potassium nitrite solution gradually dripped in. No diazotizing whatever occurred, the nitrile being recovered unchanged.

The nitrile was then dissolved in 95 per cent. alcohol, and oxides of nitrogen (from nitric acid and arsenious oxide) passed through the boiling solution. On concentrating the alcohol solution, groups of small needles separated which were dried and carefully sublimed, the sublimate melting sharply at 96.5°-97° (corr.). The yield is very small, and subliming at 98°-100° in a gentle current of air is the only method by which we have been able to get a product with a sharp melting-point.

The action of ethyl nitrite upon the nitrile was puzzling and unsatisfactory. A boiling 15 per cent. solution of the nitrite was used in large excess, with a few drops of hydrochloric acid. The solution was evaporated to dryness on the water-bath, and the residue crystallized from dilute alcohol, but no pure product could be obtained. On subliming the crude crystals on the water-bath in a gentle current of air, beautiful, white needles were obtained, the melting-point of which rose steadily with the progress of the sublimation. One crop melted at 59°-59.5° (corr.), another at 67.5°-68° (corr.), and a third at 87°-88° (corr.). Saponification of the last lot gave an acid, melting poorly at about 205°, and presumably impure 3,5-bibrombenzoic acid.

The yield in all these reactions was so small that not enough material was secured for an analysis. Conversion of the products, however, to 3,5-bibrombenzoic acid points clearly to the presence of its nitrile. The action of nitrous vapors upon the amino nitrile always gives the same product, melting sharply at 96.5°-97° (corr.), though in small yield, and we are of the opinion that this is the pure 3,5-bibrombenzonitrile, although Claus and Weil[1] report its uncorrected melting-point as 89°.

Some of this product, melting at 96.5°-97° (corr.), was saponified by heating it in a sealed tube for three hours at 170° with 75 per cent. sulphuric acid. Like its amino derivative, the bibrom nitrile tends to sublime out of the sulphuric acid and thus escape complete saponification. A short, sealed tube should, therefore, be used, as suggested. From the sealed tube, on cooling, large, glassy crystals separated which were contaminated with unsaponified nitrile. The crude bibrom acid was purified by solution in dilute caustic alkali and reprecipitation with hydrochloric acid. Crystallized from alcohol, the bibrombenzoic acid was obtained in small, glassy needles, softening slightly at 215° and melting at 218.5° (corr.). The crystals sublime quite easily. If the first crude acid is very dark in color, it may, with advantage, be recrystallized from concentrated sulphuric acid, in which it dissolves on warming and separates out unchanged on cooling.

ELIMINATION OF THE AMINO GROUP FROM 3,5-BIBROM-2-AMINOBENZOIC ACID.

The bibromanthranilic acid was dissolved in absolute alcohol, the solution heated to boiling, and saturated with nitrous gases (from nitric acid and arsenious oxide), causing the solution to assume a deep reddish brown color. The boiling solution was poured into twice its volume of water, and the light yellow precipitate filtered out and thoroughly washed with water. The crude acid thus obtained was converted into its difficultly soluble barium salt, which was purified by repeated crystallizations from water and then decomposed with hydrochloric acid. The purified bibrombenzoic acid was crystallized from benzene, and separated in radiating masses of long, white needles (m. p. 219.5°-220.5° (corr.)), similar in all its properties to the acid obtained by saponification of the bibrombenzonitrile, and evidently the 3,5-bibrombenzoic acid. The complete purification of this acid is very tedi-

[1] *Ann. Chem.* (Liebig), **269**, 223.

ous, small amounts of impurities lowering the melting-point considerably.

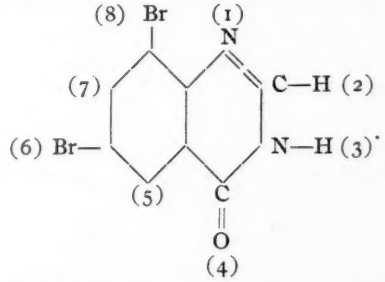
Barium Salt of 3,5-Bibrombenzoic Acid.—This was prepared by the action of baryta water upon the purified acid. It can be purified by crystallization from water, in which it is less soluble than the barium salt of the bibrom amino acid. It separates in needles of a faint yellow color. The air-dried salt was analyzed with the following results:

	Found.	Calculated for $(C_7H_3Br_2O_2)_2Ba.3\ ½\ H_2O$.
Water	8.58	8.31
Barium	18.03	18.07

Angerstein[1] gives the melting-point of 3,5-bibrombenzoic acid as 223°-227°; Hübner,[2] as 213°-214°; Claus and Weil,[3] as 209° (uncorr.). Hübner and Claus and Weil assign to the Ba salt 4 molecules H_2O; Angerstein dried the salt over H_2SO_4 and then found $2H_2O$.

SYNTHESIS OF QUINAZOLINES FROM 3,5-BIBROM-2-AMINOBENZONITRILE.

6,8-Bibrom-4-Ketodihydroquinazoline,



Three grams bibromanthranilic nitrile were heated in a sealed tube with 3 cc. glacial formic acid for five hours at 225°-235°. This temperature was much higher than necessary, as the tube was under heavy pressure when opened and the contents were black. By solution in dilute caustic soda and saturation of the alkaline liquid with carbon dioxide, a yellow precipitate separated in small amount.

[1] *Ann. Chem.* (Liebig), **158**, 10.
[2] *Ibid.*, **222**, 171.
[3] *Ibid.*, **269**, 224.

A second tube, containing 3 grams of the nitrile and 3.5 cc. glacial formic acid, was heated for sixty-nine consecutive hours at 200°-209°, and the contents worked up in the same manner. A beautiful, white crystalline substance was obtained which, after recrystallization from aniline, formed small, clear needles. The yield of pure substance was about 50 per cent. of the theoretical. It does not melt, but decomposes above 300°. On analysis, the substance gave 9 per cent. nitrogen, while the above formula requires 9.21 per cent. nitrogen.

Ethyl Ether of 6,8-Bibrom-4-Ketodihydroquinazoline.—One-half gram of the quinazoline was heated for two and a half hours in a sealed tube with slight excess of alcoholic sodium hydroxide and excess of ethyl iodide, at 100°-104°. The beautiful, crystalline product was washed with water and with alcohol, and then formed a snow-white mass of small, clear needles, melting sharply at 229°-230° (corr.). On analysis, 8.70 per cent. nitrogen was found; required for $C_{10}H_8ON_2Br_2$, 8.43 per cent.

6,8-Bibrom-2-Methyl-4-Ketodihydroquinazoline.—Two grams of the nitrile and 2 cc. of acetic anhydride were heated together for about six hours in a sealed tube at 220°-230°. By solution of the tube's contents in dilute caustic soda, fitering and saturating the filtrate with carbon dioxide, a snow-white product was obtained, which was recrystallized from aniline. By very careful heating, in a current of carbon dioxide, it may be partly sublimed in beautiful needles. It does not melt, but decomposes slowly when heated above 300°. It shows about the same solubilities as the methyl thioquinazoline (see beyond), except that it is rather more soluble in glacial acetic acid.

	Found.	Calculated for $C_9H_6ON_2Br_2$.
Nitrogen	9.14	8.81
Bromine	50.03	50.31

We have run a number of sealed tubes for the preparation of this quinazoline, varying the temperature and the duration of the heating, but in every case so far the yield has been very poor.

Ethyl Ether of 6,8-Bibrom-2-Methyl-4-Ketodihydroquinazoline.—One-half gram of the quinazoline was heated for two and a half hours at 100°-105° in a sealed tube with slight excess of alcoholic sodium hydroxide and excess of ethyl iodide. No crystals separated on cooling. The alcoholic solution was evaporated to a small

volume; the brown needles which crystallized out were recrystallized from alcohol, but still retained a slight brownish color. They began to decompose very slowly at about 170°, but did not melt at 290°.

6,8-Bibrom-2-Ethyl-4-Ketodihydroquinazoline.—Three grams nitrile and 3 cc. propionic anhydride were heated together in a sealed tube for ten and a half hours at 200°, followed by five hours longer at 210°. On treating the tube's contents with sodium hydroxide and carbon dioxide, as already described, the ethyl quinazoline was obtained as a white precipitate. Crystallized from moderately dilute alcohol, it separates in long, white, silky needles (m. p. 278°-280° (corr.)). The yield was poor.

0.2148 gram substance gave 8.10 per cent. nitrogen; required, 8.43 per cent.

6,8-Bibrom-2-Normalpropyl-4-Ketodihydroquinazoline.— Three grams nitrile and 3 cc. normal butyric anhydride were heated together in a sealed tube for ten and a half hours at 200°, followed by five hours and a half at 210°. Treatment of the tube's contents in the usual manner resulted in the separation of the N-propylquinazoline as a white, voluminous precipitate. It crystallizes from dilute alcohol in colorless, microscopic needles (m. p. 238°-240° (corr.)). The yield is only fair.

0.2351 gram substance gave 8.07 per cent. nitrogen; required, 8.09 per cent.

6,8-Bibrom-2-Isopropyl-4-Ketodihydroquinazoline. — Three grams of the nitrile and 3 cc. of isobutyric anhydride were heated together in a sealed tube for ten and a half hours at 200°, followed by five and a half hours at 210°, and then two hours longer at 220°. The tube's contents were worked up as the others were. The isopropyl quinazoline thus produced appears to the unaided eye as a white, amorphous powder, but is really a felted mass of white, microscopic, hairy crystals, which melt at 259°-260° (corr.). The yield was only fair.

0.2228 gram substance gave 7.92 per cent. nitrogen; required, 8.09 per cent.

6,8-Bibrom-2-Isobutyl-4-Ketodihydroquinazoline.—Three grams of the nitrile and 3 cc. of isovaleric anhydride were heated together in a sealed tube for ten and a half hours at 200°, five and a half hours at 210°, and two hours at 215°-220°. The tube's contents were

worked up in the usual manner, and the isobutyl quinazoline separated as a precipitate. The recrystallized substance forms colorless, microscopic needles (m.p. 230°-231.5° (corr.)). 0.1999 gram substance gave 7.82 per cent. nitrogen; required, 7.77 per cent.

Most of these brominated quinazolines decompose wholly or partly on melting. It is interesting to note that with increase in molecular weight the melting-point steadily sinks, iso compounds showing a higher melting-point than those with normal side-chains. We have already called attention to the same condition of affairs in the case of the unbrominated alkyl quinazolines and the acylated anthranilic nitriles.

These brominated quinazolines dissolve very readily in caustic alkali, but do not appear to form salts with the mineral acids.

6,8-Bibrom-2-Methyl-4-Thioketodihydroquinazoline.—Two grams of the bibromanthranilic nitrile and the calculated amount of thiacetic acid were heated together in a sealed tube for about six hours at 220°-230°. On opening the tube, slight pressure, due to hydrogen sulphide, was observed. The contents of the tube were boiled with dilute alkali, the solution cooled, filtered, and carbon dioxide passed through the filtrate, whereby a yellow, amorphous precipitate separated. Crystallized from aniline, this precipitate changed to beautiful, yellow needles. The substance does not melt at 290°, but decomposes slowly when heated. By very careful heating in a gentle current of carbon dioxide, it may be partially sublimed. It is nearly insoluble in alcohol, benzene or 50 per cent. acetic acid, slightly soluble in glacial acetic acid, and soluble in boiling aniline. It is only moderately soluble in caustic alkalies; when enough alkali is used to dissolve the quinazoline completely and a few drops of acetic acid are then added, the quinazoline is partly reprecipitated, although the solution remains strongly alkaline to litmus.

The temperature used in the first experiment (220°-230°) was unnecessarily high, as partial decomposition had occurred, and the yield of thioquinazoline was poor. Another tube, heated sixty-nine hours at 200°-209°, likewise showed too much decomposition. A third tube, heated forty-two hours at 180°, was much more satisfactory in appearance; but little decomposition had occurred, and a yield of 2.1 grams of the pure thioquinazoline was obtained from 3 grams of the bibromnitrile.

Analysis of 6,8-Bibrom-2-Methyl-4-Thioketodihydroquinazoline.—The determination of carbon and hydrogen in this bibrom-thioquinazoline proved exceedingly troublesome, on account of the high percentage of bromine (nearly 48 per cent.) and the presence of sulphur.

The de Roode mixture of red lead and lead chromate was used as the oxidizing agent, and it was found to be much more efficient with freshly prepared lead chromate than with the commercial fused article. Freshly precipitated and thoroughly washed lead chromate was mixed with red lead and made into little balls. These were dried, ignited in an open dish, and then thoroughly burned out in a stream of dry oxygen. As thus prepared, they did not melt or disintegrate.

A long combustion tube was used, in which were placed an oxidized copper gauze, then a long porcelain boat containing the thioquinazoline mixed with ignited red lead and covered with the same, then a short, silver spiral, followed by the oxidizing mixture, a long, silver spiral, and a bright copper gauze. The combustion was conducted very slowly at a moderate temperature. Unless the temperature of the exit end of the tube was kept well down, bromine could be detected in the gases passing into the absorption train.

	Found.	Calculated for $C_9H_6N_2SBr_2$.
Carbon	32.94–32.76	32.33
Hydrogen	2.01–2.03	1.80
Nitrogen	8.70–8.52	8.38
Sulphur	9.64	9.58
Bromine	47.79	47.91

Ethyl Ether of 6,8-Bibrom-2-Methyl-4-Thioketodihydroquinazoline.—This was prepared by the method already described for the corresponding oxygen compound. The product crystallized out of the sealed tube on cooling. Washed with water and with alcohol, it appeared in beautiful, light yellow needles, which began to decompose at about 305°, but did not melt completely at 360°.

ORGANIC LABORATORY, HAVEMEYER HALL,
COLUMBIA UNIVERSITY,
July, 1903.

[CONTRIBUTION FROM THE LABORATORY OF THE LOUISIANA AGRICULTURAL EXPERIMENT STATION.]

A CONTRIBUTION TO THE CHEMISTRY OF RICE OIL.

BY C. A. BROWNE, JR.

Received January 2, 1900.

I. THE CHEMICAL AND PHYSICAL CONTENTS OF RICE OIL.

BUT very little attention has been paid thus far to the chemistry of rice oil, notwithstanding the very extensive use of rice as a food product. The only data, which the writer has been able to find, is a report by Smetham[1] upon an oil obtained from Rangoon rice-meal by hydraulic pressure, the meal containing about 15 per cent. oil. The oil, as thus expressed, had a dirty green color, and was partly solid at the ordinary temperature. It appeared to be especially remarkable for the large proportion of free fatty acids present, the percentage of which ranged from 31.6 to 77.2. A saponification value of 193.2 and an iodine absorption of 96.4 were also reported.

In connection with some investigations recently carried out at the Louisiana Experiment Station in New Orleans, upon rice and the various by-products of the rice-milling industry, some attention was paid to rice oil. A number of oil samples were examined, including the oil extracted from the rice itself, as well as that obtained from the bran or meal. The latter comprises the gluten layer and germ of the rice grain and, when unadulterated with hulls, contains nearly 15 per cent. oil.[2]

The chemical and physical constants of an oil obtained from a sample of rice bran are given in the following table:

TABLE I.—CONSTANTS OF RICE OIL.

Specific gravity $\frac{99^\circ}{99^\circ}$	0.8907
Melting-point (point of liquefaction)	24°
Acid number	166.2
Saponification number	193.5
Ether number	27.3
Iodine number	91.65
Reichert-Meissl number	1.1
Mean molecular weight of insoluble fatty acids	289.3
Melting-point of insoluble fatty acids	36°

The above oil was semisolid in consistency during the winter;

[1] *J. Soc. Chem. Ind.* (1893), p. 848.

[2] Calculating the rice-meal to a water-free and starch-free basis, there would be about 20 per cent. oil in the pure gluten and germ.

it began to melt at about 24°, but did not become perfectly transparent until 47°. During the warm summer, the oil liquified partly and consisted then of a brownish-colored oil with a deposit of crystallized fats. The high acid number is noteworthy, corresponding to 83.5 per cent. of free oleic acid. In this respect the oil shares the peculiarity of those analyzed by Smetham. The fact that rice oil contains fats of high melting-point and fatty acids of high mean molecular weight would indicate the probable presence of such higher homologues as arachidic, behenic or lignoceric acids. This supposition was strengthened by the granular deposit of insoluble soaps which settled out after saponifying the oil with alcoholic potash. Further researches as to the constitution of rice oil are greatly to be desired.

II. THE CAUSES PRODUCING ACIDITY IN RICE OIL.

In studying the feeding value of different rice products, our attention was called to the fact that animals frequently showed a marked distaste to rice bran or meal as a food. An inquiry into the cause of this showed that in such cases the feed was very rancid and that this rancidity was due to the very acid condition of the rice oil. Experiments made upon fresh rice bran showed that the oil from the same was only slightly acid, but that upon standing any great length of time a rapid development of acidity took place in the oil, the feed at the same time becoming rancid. In large bulks the development of rancidity in rice-meal seems to be accompanied by a heating and caking of the material.

Instances of such excessive acidity as those noted for rice oil, have been observed in the case of a few other vegetable oils. Palm oil is especially characterized by a high content of free acid. Lewkowitsch[1] states that "even in the fresh state the proportion of fatty acids in palm oil, calculated as palmitic acid, amounts to 12 per cent., and may in older samples reach as much as 100 per cent.—in other words, the splitting-up of the glycerides may become complete." Olive kernel oil[2] and olive oil[3] expressed from the marc also contain large quantities of free fatty acids.

It has long been a recognized fact that atmospheric oxygen, especially in the presence of light, is a very important factor in the decomposition of oils and fats. This influence would no doubt

[1] Lewkowitsch : "Analysis of Oils, Fats, and Waxes," 2nd edition, p. 517.
[2] Benedikt : "Analyse der Fette und Wachsarten," 3 Auf., p. 458.
[3] *Ibid.*, p. 447 ; see also Lewkowitsch : *Loc. cit.*, p. 451.

be greater with oil in a finely divided condition, as would be the case in rice meal. There is, however, another explanation possible for the decomposition of rice oil besides that of oxidation. The work of different investigators shows that in many cases a decomposition of vegetable oil is produced by means of a fat-splitting enzyme—*lipase*. Reynolds Green[1] has reported the presence of lipase in the germinating seeds of the castor oil plant and Sigmund[2] has demonstrated its existence in both the resting and germinating seeds of rape, poppy, hemp, flax and maize. The crushed seeds of these plants produced in all cases a development of acidity in neutral emulsions of oil. That the hydrolysis of the oil was due to an enzyme, was shown by the fact that control experiments, in which the enzymes had been killed by boiling, developed no acidity. The high degree of acidity in palm oil and olive-marc oil has also been attributed to enzyme action.[3]

LIPASE IN RICE BRAN.

An aqueous extract of rice bran was prepared by allowing 20 grams of the material to soak in 100 cc. of cold water for several hours. 25 cc. of the clear filtered extract, when mixed with 5 cc. of commercial hydrogen peroxide, produced a rapid evolution of oxygen, the quantity of this exceeding 100 cc. within a few minutes. The bran extract also produced with tincture of guaiac a strong blue coloration, after adding a few drops of hydrogen peroxide. Both of the above reactions failed with bran extract which had been boiled. Many plant juices and extracts cause a catalytic decomposition of hydrogen peroxide, and give the blue reaction with guaiac and the peroxide; these properties have been thought by some investigators to belong to nearly all enzymes, though Loew[4] considers them characteristic of two special ferments, *catalase* and *peroxidase*. Without entering into a discussion of this question, we may say that the above reactions, while showing that enzymes are present in rice, do not throw much light upon their specific nature or functions.

To determine whether or not a lipatic ferment is present in rice bran, use was made of the well-known emulsion test. Twenty

[1] Reynolds Green : "Soluble Ferments and Fermentation," p. 227.

[2] Sigmund : "Ueber fettspaltende Fermente im Pflanzenreiche," *Monatsh. Chem.* (Vienna), **11**, 272 (1890).

[3] Lewkowitsch : "Notes on Fat-Splitting Enzymes," *J. Soc. Chem. Ind.* (1903), p. 69.

[4] Loew: "Catalase, a New Enzyme of General Occurrence," Report No. 68, U. S. Dept. of Agr.; see also Report No. 65 by same author, "Physiological Studies of Conn. Leaf Tobacco," pp. 30-34.

cc. of the clear bran extract were thoroughly shaken up with an equal volume of a thick emulsion of castor oil, and the mixture rendered faintly alkaline to litmus solution. After standing at the laboratory temperature for twenty-four hours, the solution began to turn pink, and in two days had become a deep red. A similar experiment, conducted with extract which had been previously boiled, remained alkaline; likewise, blanks of the unboiled extract to which no emulsion had been added, so that the development of acid could only come from the action upon the oil of a fat-splitting enzyme. To prevent the formation of acid products by bacteria, 0.25 per cent. of potassium cyanide was used in each experiment as a germicide. The cyanide may have exerted an inhibitive effect upon the activity of the enzyme, yet the necessity of using an antiseptic agent in such tests is imperative, as was shown by the fact that, when no cyanide was employed, neutral solutions of bran extract became acid to litmus in a few hours. After standing a week, the acid emulsion in the above experiment was shaken out with ether, and the ethereal solution filtered and evaporated to dryness. The oil thus obtained had an acid number of 29.7, which would indicate that about 16 per cent. of the oil had undergone hydrolysis.

To determine the hydrolyzing effect of lipase upon rice oil under natural conditions, the following experiment was conducted. A sample of fresh rice bran was taken to the laboratory immediately after milling and divided into two portions. One portion was subjected to a dry heat of 90° C to destroy any enzymes; the other portion remained untreated. Both samples were tied up in sacks and set aside for one month. The acidity of the oil from the fresh bran (containing 14.3 per cent. oil) was determined, and also that of the oil obtained from the raw rice used in manufacturing the bran. The same determinations were also made on the oils extracted from the two samples of bran after standing one month. The results of the work are given in the following table:

TABLE II.

Source of oil.	Acid number.	Free acid as oleic. Per cent.
Raw rice	13.8	6.9
Fresh bran (six hours after milling)	24.7	12.5
Bran, one month old, unheated	123.8	62.2
" " " " heated	47.0	24.0

The above results show that an exceedingly rapid decomposi-

tion of the oil in the unheated bran had taken place. In the oil of the bran, which had been heated, there was also some development of free acid, but the quantity formed was less than one-fourth that developed in the oil of the unheated sample. The experiment would indicate that while the development of acidity in rice oil may be, to a slight extent, the result of oxidation, it is to a much greater degree the effect of a fat-splitting enzyme.[1]

The sample of raw rice, from which the bran used in the experiment was made, was taken from a large quantity that had been lying in storage in a New Orleans warehouse many months. The oil from the bran six hours after milling, compared with the oil from the original rice, shows an increase in free acid of 5.6 per cent. This shows that a rapid decomposition of the rice oil sets in immediately after milling, the activity of the enzyme[2] seeming thus to depend upon an exposure of the oil-bearing tissues of the rice grain to the air. The amount of free acid in the oil within the rice grain is probably less than that indicated in Table II, as some decomposition no doubt took place during the grinding of the grain, before the extraction with ether.

The foregoing experiments have a certain practical interest, since a destruction of the lipase at once suggests itself as a means for the prevention of rancidity in rice-meal and similar products. By subjecting the material, directly after milling, to a dry heat sufficient to destroy the enzyme, such as is done in the kiln-drying of certain feeds, the development of rancidity would be largely checked.

III. THE DIGESTIBILITY OF RICE OIL.

In connection with some feeding experiments, recently conducted at this Experiment Station, with rice bran and rice polish, the following coëfficients of digestibility for rice oil were obtained. Two steers were used in the work.

	Rice bran. Per cent. oil digested.	Rice polish. Per cent. oil digested.
Steer No. 1	52.0	66.0
" " 2	57.5	81.2
Average	54.8	73.6

There are several facts which may explain the greater digesti-

[1] For further particulars as to the action of lipase, see the work of Kastle and Loevenhart (*Amer. Chem. J.*, **24**, 491 (1900)).

[2] The enzyme is probably the product of an antecedent substance or *zymogen*, this transformation not taking place except when the seed is crushed or while it is germinating. (See Reynolds Green, "Soluble Ferments and Fermentation," p. 381.)

bility of the rice oil in the polish. In the experiment with rice polish, the steers received only about one-third the quantity of oil given in the bran experiment and may thus have been able to digest a greater percentage of oil from the ration. The bran was very coarse, containing about 30 per cent. of rice hulls; the polish was free from hulls, and contained more of the starchy part of the rice than the bran. The oil from the bran contained 83.5 per cent. free fatty acids, the oil from the polish 47.5 per cent. The conditions may, therefore, have been more favorable in the polish towards securing a more complete digestion of the oil. Individuality of the animal is seen to play an important part. Steer No. 2 digested a greater percentage of oil in both experiments, the difference in the case of the polish being especially marked.

In the bran experiment, the oil from the feed and the undigested oil from the feces were analyzed. A comparison of the two sets of constants shows very noticeable differences, and throws some light upon the changes which the rice oil undergoes during digestion.

TABLE III.—SHOWING EFFECT OF DIGESTION UPON COMPOSITION OF RICE OIL.

Constant.	Oil from rice bran.	Oil from feces of steers fed on rice bran.
Melting-point (point of liquefaction)	24°	58°
Acid number	166.2	144.2
Saponification number	193.5	176.0
Ether number	27.3	31.8
Iodine number	91.65	27.08
Mean molecular weight insoluble fatty acids	289.3	320.2
Melting-point insoluble fatty acids	36°	60°

The oil obtained from the feces was light-colored and of wax-like consistency. The soaps obtained on saponifying this oil with alcoholic potash were marked by a low degree of solubility in alcohol. The oil extracted from the feces was no doubt contaminated to some extent with metabolic products from the animal, such as biliary substances and fatty bodies from the intestines. Some unsaponifiable matter was present, but this was removed before determining the constants of the fatty acids. Beef-fat from the intestines, according to Mayer,[1] has the following constants:

[1] Wagner's *Jahresberichte* (1880), 844.

Melting-point	50°
Saponification number	196.2
Melting-point insoluble fatty acids	47.5°
Mean molecular weight insoluble fatty acids	278.2

The presence of fat, sluffed off from the walls of the intestinal tract, could not, therefore, explain the differences noted in Table III. The most satisfactory and plausible explanation of the facts is a difference in digestibility of the various constituents of the rice oil. The liquid unsaturated bodies are very largely absorbed in the process of digestion, as is shown by the marked decrease in the iodine number. The fatty acids of lowest molecular weight are also the easiest to assimilate; hence, the oil excreted in the feces consists largely of a residue of acids of high mean molecular weight and high melting-point. Reference was made, in the first section of this paper, to the probable presence in rice oil of such higher acids as arachidic, behenic, or lignoceric, and this supposition finds support in the character of the fatty acids in the oil from the feces, these having a mean molecular weight higher even than the molecular weight of arachidic acid (312).

Stearic acid, the highest saturated fatty acid in the animal body, has a molecular weight of 284, and saturated fatty acids of greater molecular weight than stearic are probably assimilated by the animal only to a limited extent.

In conclusion, the writer desires to express his indebtedness to Dr. W. C. Stubbs, under whose direction the work was carried on, for advice and encouragement.

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OLIVE OILS AND OLIVE OIL SUBSTITUTES.

BY L. M. TOLMAN AND L. S. MUNSON.

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SOURCES OF THE OILS.

IN AN investigation of olive oils and their substitutes, a number of pure California and Italian olive oils were obtained and analyses of them made. The California oils were largely obtained from representative producers, with affidavits as to their purity. The Italian oils were received through agents in Italy. The collection of oils thus made contained samples from most of the oil-producing districts of both countries.

The varieties of olives used are given, to a certain extent, with California oils, but with the Italian oils it was impossible to obtain this information. The methods of analysis used were those given in the U. S. Dept. of Agriculture, Bureau of Chemistry, Bulletin 65, pp. 20-35.

FATTY ACIDS.

By liquid fatty acids are meant the acids, the lead soaps of which are insoluble in ether, and by the solid fatty acids, those the lead soaps of which are insoluble in ether. This method of separation, while not absolutely exact, gives a very close approximation of the amounts of saturated or solid fatty acids and unsaturated or liquid fatty acids. The iodine number of the liquid fatty acids was determined exactly as with the Hübl method on oils. Great care is necessary in drying the liquid fatty acids to prevent oxidation and in this work they were dried at about 70° C., in a current of coal gas.

TABLES OF ANALYSES.

In Table I are the analyses of thirty-eight samples of California olive oil and eighteen samples of Italian olive oil. These are mostly virgin or first-pressing oils, but a few oils have been included which cannot be classed as edible oils. These are not included in the average or maximum and minimum, but are given in order to show what widely varying results may be obtained with pure oils, and that the cause of these abnormal results would not be detected unless the determination of free acids was made. The amount of free acids present in an oil affects the specific gravity and index of refraction to a marked degree. Sample No. 22,619, with an index of refraction of 1.4672 and 44.40 per cent. of free acid, and No 673 with specific gravity of 0.9149 and 12.11 per cent. of free acids are examples of this fact. It seems very probable that some of the very low figures on these determinations, reported by various analysts, would be explained if the free acid had been determined.

DISCUSSION OF ANALYTICAL DATA.

An examination of Table I will show that on the high-grade oils there is only a very small variation in specific gravity and index of refraction for both the California and Italian oils. The wide range in Maumené figures means nothing, as different strengths of acid were used, but the specific temperature figures

TABLE I, PART I—PURE CALIFORNIA OLIVE OILS.

Serial No.	Variety and locality.	Specific gravity at 15.5° C.	Butyro-refractometer reading at 15.5° C.	Index of refraction at 15.5° C.	Maumené number.	Specific temperature reaction.	Hübl number.	Iodine number of liquid fatty acids.	Saponification number.	Melting-point of fatty acids. °C.	Solid fatty acids. Per cent.	Free fatty acids as oleïc. Per cent.
23,692	Mission olive, Chico	0.9168	68.5	1.4713	...	....	85.6	96.6	191.2	22.6	5.12	0.95
23,463	" " Concord	0.9164	68.4	1.4712	48.0	106.6	85.6	91.5	191.9	21.3	4.92	0.79
22,713	" " Santa Barbara	.....	68.7	1.4715	...	....	85.3	94.9	191.1	22.4	5.11	0.73
22,714	" " " " [1]	.....	68.5	1.4713	...	....	84.6	...	191.5	22.4	3.87	1.26
22,715	" " " " [2]	.....	68.2	1.4711	...	....	84.7	...	191.3	20.5	2.02	2.73
23,458	" " " "	0.9169	68.7	1.4715	48.4	107.5	88.2	94.9	191.4	23.5	4.42	0.73
838	" " San Diego	0.9169	69.2	1.4718	49.5	108.5	86.2	...	190.6	24.0	6.15	1.07
839	" " " "	0.9171	69.2	1.4718	48.4	106.0	89.0	...	189.9	21.2	4.94	3.51
840	" " " "	0.9169	68.9	1.4716	48.2	105.7	86.3	...	189.4	24.0	5.94	1.09
23,457	" " Santa Clara	0.9166	68.3	1.4711	47.0	104.4	86.2	91.2	191.6	21.1	3.39	0.97
832	" " " "	0.9173	68.8	1.4715	47.6	100.1	84.9	...	189.3	20.5	5.40	0.85
834	" " " "	0.9168	68.8	1.4715	46.2	97.2	84.5	...	189.3	19.4	6.03	0.34
23,605	" " Santa Barbara	0.9171	68.5	1.4713	47.1	104.2	88.5	94.5	191.5	20.2	2.43	1.54
798	" " " "	0.9177	68.8	1.4715	51.0	107.3	89.7	...	190.0	19.2	...	0.63
795	" " " "	0.9177	69.0	1.4717	50.0	105.2	89.7	...	189.8	19.8	4.73	0.75
796	" " " "	0.9177	68.8	1.4715	52.1	109.7	89.8	...	189.9	19.2	4.69	0.61
797	" " " "	0.9177	68.8	1.4715	50.2	105.6	89.8	...	189.7	19.6	5.44	0.63
22,617	Redding picholine olive, Berkeley[3]	67.3	1.4706	...	....	78.5	...	194.4	30.2	...	0.36
23,462	picholine olive, Oroville ..	0.9162	66.9	1.4703	43.0	95.5	79.9	91.7	192.2	31.0	10.91	0.79

[1] Second pressing.

[2] Common grade of oil for lubricating.

[3] Made in 1893.

TABLE I, PART I (*Continued*)—PURE CALIFORNIA OLIVE OILS.

TABLE I, PART I (*Continued*)—PURE CALIFORNIA OLIVE OILS.

Serial No.	Variety and locality.	Specific gravity at 15.5° C.	Butyro-refractometer reading at 15.5° C.	Index of refraction at 15.5° C.	Maumené number.	Specific temperature reaction.	Hübl number.	Iodine number of liquid fatty acids.	Saponification number.	Melting-point of fatty acids. °C.	Solid fatty acids. Per cent.	Free fatty acids as oleic. Per cent.
23,461	Picholine olive, Guerneville.....	0.9162	67.5	1.4707	45.0	100.0	83.0	92.4	192.0	28.0	7.62	1.07
22,619	Manzanillo olive, Berkeley[1],[2]	.....	62.0[3]	1.4672	...	....	79.6	...	191.8	24.5	...	41.40
23,456	Italian varieties olive, Santa Clara .	0.9169	68.3	1.4711	47.7	106.0	84.3	93.4	191.9	23.4	7.23	0.53
831	" " " " " .	0.9168	68.8	1.4715	46.6	98.1	85.2	...	189.3	20.6	...	0.61
833	" " " " " .	0.9170	68.8	1.4715	48.0	101.0	84.8	...	189.8	20.2	6.55	0.65
506	Mixed varieties olive, Los Angeles	0.9174	68.5	1.4713	38.0	98.9	84.4	...	193.1	22.4	...	0.71
836	" " " " "	0.9174	68.8	1.4715	48.2	105.7	86.0	...	190.7	24.8	...	2.51
837	" " " " "	0.9167	68.4	1.4713	45.0	98.6	84.2	...	190.3	23.6	5.16	0.51
835	" " " " "	0.9167	68.2	1.4711	44.8	98.2	82.7	...	190.4	26.0	6.19	0.96
21,091	" " " Cloverdale .	0.9167	68.8	1.4715	45.3	94.5	81.9	...	190.0	26.6	12.96	1.42
3,460	" " " Yolo	0.9167	68.2	1.4711	47.0	104.0	85.7	93.8	190.4	23.4	6.24	2.24
22,618	Mixed olives, Berkeley[2]	.....	67.5	1.4707	...	....	83.7	...	192.5	20.7	...	8.21
23,124	" " Redlands	0.9171	68.2	1.4711	45.5	...	83.7	92.5	193.3	25.4	6.20	0.47
841	" " "	0.9168	68.8	1.4715	47.1	98.3	86.9	...	189.4	21.6	8.61	0.20
842	" " "	0.9168	68.7	1.4715	46.8	97.7	87.2	...	189.5	21.4	7.52	0.21
843	" " "	0.9169	68.6	1.4714	45.6	95.2	85.1	...	189.6	22.8	4.33	0.28
23,459	" " Napa	0.9162	67.7	1.4709	45.5	101.2	82.9	90.3	191.6	25.0	5.69	1.72
673	" " " [3].....	0.9149[2]	66.4	1.4699	45.5	95.0	83.3	...	189.5	21.6	7.58	12.11
23,649	" " Oroville	0.9164	68.0	1.4710	43.5	96.6	83.4	88.9	192.1	22.6	...	1.43

[1] Poor quality.

[2] Not included in the average on account of high percentage free acid.

[3] Second pressing.

TABLE I, PART II.—PURE ITALIAN OLIVE OILS.

Serial No.	Locality.	Specific gravity at 15.5° C.	Butyro-refractometer reading at 15.5° C.	Index of refraction at 15.5° C.	Maumené number.	Specific temperature reaction.	Hübl number.	Iodine number of liquid fatty acids.	Saponification value.	Melting-point of fatty acids. °C.	Solid fatty acids. Per cent.	Free fatty acids as oleic. Per cent.
580	Bari	0.9177	67.9	1.4709	39.6	103.1	81.8	...	191.7	28.5	....	....
933	Puglia	0.9158	67.7	1.4708	43.5	95.6	80.4	94.8	192.0	26.2	16.47	1.02
960	Bari	0.9159	67.6	1.4707	41.7	101.8	80.9	96.0	191.4	26.6	16.87	0.80
961	Bitonti	0.9162	67.6	1.4707	43.5	95.6	80.8	96.5	191.7	27.3	13.67	0.69
935	Puglia	0.9162	67.7	1.4708	44.2	97.1	80.5	95.1	191.9	29.3	15.20	1.03
936	"	0.9155	67.7	1.4708	44.8	98.4	81.8	96.2	191.5	26.2	11.07	2.79
962	Bari	0.9159	67.6	1.4707	43.5	99.1	81.2	96.5	191.8	27.9	17.72	0.62
931	Toscanja	0.9166	67.6	1.4707	44.4	97.4	80.7	89.8	189.6	25.8	5.01	0.82
932	Lucca	0.9167	67.5	1.4707	44.4	97.4	80.5	...	190.1	25.2	8.07	0.80
958	" [1]	0.9158	68.0	1.4710	48.0	102.3	81.8	90.6	190.4	22.9	6.04	0.79
959	" [2]	0.9164	68.0	1.4710	46.2	98.4	81.5	92.0	190.5	23.9	7.95	0.63
934	Geneo	0.9159	67.6	1.4707	42.5	96.8	81.1	92.4	190.6	24.5	8.60	0.92
952	Liguria	0.9160	68.0	1.4710	45.0	97.9	81.4	90.5	190.1	21.6	7.38	0.61
953	"	0.9161	67.3	1.4705	47.0	100.0	79.2	90.8	191.3	24.9	9.76	1.18
954	"	0.9180	68.5	1.4713	48.3	103.0	86.1	97.5	190.5	25.0	7.76	2.55
955	"	0.9157	67.8	1.4709	44.2	97.1	82.6	94.8	190.8	23.5	8.93	1.09
957	"	0.9166	68.0	1.4710	45.0	97.9	82.1	91.1	189.7	21.6	5.53	1.90
956	Abruzzi	0.9164	68.3	1.4712	49.1	104.7	84.5	98.4	190.7	28.5	13.51	0.57
	California oils { Average	0.9168	68.2	1.4711	46.8	101.6	85.1	92.8	190.6	22.5	....	0.85
	California oils { Maximum	0.9180	69.2	1.4718	52.1	109.7	89.8	99.6	194.6	31.0	12.96	3.51
	California oils { Minimum	0.9162	66.9	1.4703	38.0	94.5	78.5	88.9	189.3	19.2	2.02	0.20
	Italian oils... { Average	0.9163	67.8	1.4709	44.9	99.1	81.5	94.0	....	25.4	....	1.11
	Italian oils... { Maximum	0.9180	68.5	1.4713	49.1	104.7	86.1	98.4	192.0	29.3	17.72	2.79
	Italian oils... { Minimum	0.9155	67.3	1.4703	39.6	95.6	79.2	89.8	189.6	21.6	5.01	0.57

[1] First grade. [2] Second grade.

do not show such a wide variation. The average for California oils is a little higher, due probably to the higher iodine value of the oils examined. The reason for including the figures given by the Maumené test is that the specific temperature figures are affected to a certain degree by the strength of the acid, as was shown by the work of Sherman, Danziger and Kohnstamm.[1] This will account for the somewhat lower specific temperature numbers obtained by De Negri and Fabris,[2] and Milliau, Bertainchand and Malet[3] on French and Algerian oils, as they used an acid which gives a rise of temperature with water of about 36° to 37° C., while the acid used in this work gives a rise of from 45° to 46° C.

The variation found in the Hübl numbers of the oils is very wide and the same is true with the iodine figures on the liquid fatty acids. The variation in the Hübl figures is, to a considerable extent, controlled by the amount of solid fatty acids present, but is also affected by the composition of the liquid fatty acids, as the wide variation in the iodine absorption of these acids shows. The Italian oils are not very different from the California oils in this particular, and this work is confirmed by De Negri and Fabris[4] in their recent extensive work on Italian oils.

These results make it evident that the iodine absorption alone can have little value in determining the purity of an oil, as all but very gross adulteration can be covered up by this range of from 78.5 to 89.8 for the Hübl figures. The average for the Hübl figures on the oils examined is higher for the California oils than for Italian oils, but from all the figures available on pure oils there is not so wide a difference. De Negri and Fabris[4] found an average of 83.7. In fifty-seven samples of commercial Italian olive oil, imported into this country, in which no adulteration was detected, the average figure was 80.5.

The melting-point of the fatty acids—the point where the acids in a capillary tube became clear—also showed wide variation and a very close relation tc the percentage of solid fatty acids, as would be expected. These oils were all tested qualitatively for cotton-seed, peanut and other seed oils, with negative results in all cases.

[1] This Journal, **24**, 266.
[2] "Ann. Lab. chim. Cent. delle Gab.," Vol. I, Gli Olii, Part I.
[3] "Rap. sur les Huiles D'Olive de Tuniise," 1900.
[4] *Loc. cit.*

TABLE II.

Serial No.	Kind of oil.	Specific gravity at 15.5° C.	Butyro-refractometer reading at 15.5° C.	Index of refraction at 15.5° C.	Maumené number.	Specific temperature reaction.	Hübl number.	Iodine number of liquid fatty acids.	Saponification value.	Melting-point of fatty acids. °C.	Solid fatty acids. Per cent.	Free fatty acids as oleic. Per cent.
773	Cocoanut	0.9259	49.1	1.4587	21.0	44.0	8.58	31.9	259.5	25.2	65.90	0.11
494	Palm	0.9128	...	.....	...	...	53.0	99.0	201.0	49.2	....	19.53
22,433	Lard	0.9148	67.4	1.4706	47.8	106.2	75.9	94.0	195.7	33.2	18.90	0.75
23,606	"	0.9160	69.5	1.4720	46.5	103.3	69.7	95.8	197.7	38.4	26.68	0.28
499	Peanut[1]	0.9186	70.0	1.4723	46.5	129.1	87.8	...	191.8	34.3	....	0.40
772	" [2]	0.9188	71.3	1.4431	63.2	135.3	96.3	114.6	189.9	36.4	....	0.24
495	Mustard. Black mustard	0.9170	76.5	1.4762	68.2	189.4	105.8	....	176.0	21.5	4.05	0.38
770	Brown "	0.9184	76.2	1.4760	77.6	165.4	110.4	114.2	178.5	20.6	1.06	0.48
771	Black "	0.9193	76.5	1.4762	79.4	169.3	113.0	119.8	182.8	20.8	2.32	0.34
776	Yellow "	0.9147	74.5	1.4750	61.4	130.9	98.4	103.1	173.0	21.0	tr	0.13
496	Rape	0.9143	74.3	1.4749	54.9	152.5	92.7	101.5	174.7	21.9	1.02	0.63
775	"	0.9163	74.1	1.4748	63.6	135.6	101.3	105.1	176.6	20.5	tr	1.26
1,187	Almond	0.9186	70.9	1.4728	45.3	117.6	96.2	....	192.5	23.2	...	0.48
23,624	Sunflower	0.9201	72.7	1.4739	...	....	108.3	113.8	192.3	21.0	3.67	0.18
498	"	0.9205	72.1	1.4736	60.0	166.7	104.1	....	191.2	21.0	4.12	1.72
777	Maize	0.9253	77.5	1.4768	89.2	190.2	123.3	134.5	189.9	21.6	7.44	3.65
1,186	Cottonseed	0.9236	75.6	1.4757	67.1	174.3	110.9	....	198.5	38.0	...	2.17
1,159	" " butter oil "	0.9226	72.5	1.4738	66.4	172.9	103.8	143.0[3]	197.1	35.5	22.90	0.07
1,160	" " summer white "	0.9226	72.3	1.4737	73.4	191.1	106.2	145.4[3]	196.9	39.0	22.43	0.07
1,161	" " cooking oil "	0.9226	72.3	1.4737	66.2	172.4	104.8	145.7[3]	196.0	39.6	23.60	0.04
774	Poppy	0.9244	77.8	1.4770	75.8	213.0	134.9	142.0	193.8	25.8	6.67	0.90
1,188	Linseed	0.9318	88.8	1.4831	...	....	179.5	....	191.7	19.2	3.88	0.40

[1] 3.78 per cent. arachidic acid, melting-point, 72.5° C.

[2] 4.12 per cent. arachidic acid, melting-point, 72.0° C.

[3] Iodine value calculated.

Table II contains the results of analysis of a number of pure oils of various kinds, some of which were pressed in the laboratory and others were pressed under our supervision. The lard oils were obtained from Armour & Co., and cottonseed oils, except No. 1,186, from the American Cotton Oil Company. The lard oil No. 23,606 was a pure white product and free from lardy odor, except when heated. The peanut oils were cold-pressed from American nuts. The cocoanut oil was from fresh cocoanuts.

The mustard, rape and poppy oils were prepared from seeds which were identified by Miss Charles, of the Seed Laboratory of the U. S. Dept. of Agriculture, as follows:

770	Brown mustard	*Brassica Arvensis* (Charlock).
771	Black "	*Brassica Juncea* (Indian mustard).
776	Yellow "	*Sinapus Alba* (yellow mustard).
775	Rape seed	*Brassica Napus.*
774	Poppy seed	*Papaver somnifer* (opium poppy).

The other oils were prepared from commercial seeds or nuts and were cold-pressed. These oils, with the exception of linseed, are used as substitutes or adulterants of olive oil and were analyzed in order to obtain more complete data on American oils, there being very few published results on oils of this class.

The Maumené test was made on the oils having a high iodine number by using a weaker acid, as suggested by Sherman, Danziger and Kohnstamm.[1]

The relation between the solid fatty acids, the Hübl number and the iodine number of the liquid fatty acids should be noted. The mustard oils have a higher Hübl number than cottonseed-oil, but having only a small percentage of solid fatty acids, the true iodine number, as it is sometimes called, is only a little higher than the Hübl number, while the cottonseed-oils, with a large percentage of solid fatty acids, have a much higher iodine figure for the liquid fatty acids.

The relation of the iodine number of the liquid fatty acids to the drying properties of the oil is shown to the greatest extent in cottonseed and poppy oils. The iodine numbers of the liquid fatty acids of the two oils are practically the same and their drying properties are practically the same, but the Hübl number of poppy oil is 134.9 and cottonseed-oil 103-105. In this case, the Hübl number gives very little idea as to the drying capacity of the oil. This same relation holds true with other oils. Rape oils and cottonseed-

[1] This Journal, **24**, 266.

oil with the same Hübl number have very different powers of absorbing oxygen.

The true iodine figure gives a much better idea of the nature of the unsaturated fatty acids present than the Hübl figure. Sample No. 23,606, with a Hübl number of 69.7, but containing 26.68 per cent. of solid fatty acids, has an iodine number of the liquid fatty acids of 95.8, which is practically the same as that given by olive oils, showing that the liquid portion of lard oil is very similar to the liquid portion of olive oil.

The Hübl figure depends largely on the method of making the oil, whether hot- or cold-pressed. The unsaturated fatty acids of the cocoanut oil are very different from those of the palm oil, the former having an iodine figure of 31 and the latter, of 99. This figure closely agrees with that of oleic acid, the unsaturated acid of lard and olive oils.

The iodine number of liquid fatty acids can be calculated from the iodine number of the oil and the per cent. of solid fatty acids, if one assumes that the total fatty acids in an oil is 95.5 per cent.

The total fatty acids less the solid fatty acids give the liquid fatty acids. From the following formula, the iodine number of the liquid fatty acids can be calculated:

$$A = \frac{I\ 100}{L}$$

A = Iodine number liquid fatty acids.

I = Hübl number.

L = Percentage liquid fatty acids.

The peanut oils Nos. 499 and 772 show quite a difference in iodine number, but it can be seen that a very large amount of either of these oils could be mixed with olive oil without changing any of the physical or chemical properties enough to certainly show its presence.

The only reliable test is the separation of the arachidic acid. These two samples had 3.78 and 4.12 per cent. of this acid present, which melted at from 72° to 72.5° C.

In all of these oils, even those taken fresh from the press, free fatty acids were found, showing that they must have existed as such in the seeds. The three samples of commercial cottonseed-oil contained only traces of free acid due to the process of refining, while sample No. 1,186, which had not been refined, but was fresh from the press, contained 2.17 per cent.

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, LABORATORY OF INSECTICIDES AND AGRICULTURAL WATERS, U. S. DEPARTMENT OF AGRICULTURE. No. 51. SENT BY H. W. WILEY.]

A MODIFICATION OF THE AVERY-BEANS METHOD FOR DETERMINING TOTAL ARSENIOUS OXIDE IN PARIS GREEN.

BY J. K. HAYWOOD.

Received June 26, 1903.

INTRODUCTION.

UNTIL recently, nearly all methods for determining total arsenious oxide in Paris green, in so far as the author has been able to find by careful search of chemical literature, were based upon the oxidation of all arsenic to the "ic" condition and a subsequent precipitation with magnesia mixture, followed by a gravimetric determination as magnesium pyroarsenate. Some oxidized with hydrochloric acid and potassium chlorate and determined the arsenic in the presence of copper; some oxidized with fuming nitric acid and determined the arsenic in the presence of copper, and others first removed the copper by boiling with sodium hydroxide and oxidized the filtrate with hydrochloric acid and potassium chlorate, but all finally precipitated the arsenic with magnesia mixture and weighed as magnesium pyroarsenate.

While a few chemists determined the arsenic by precipitation along with copper as the sulphide and a subsequent separation of the two sulphides, this method, on account of inherent difficulties, was seldom employed.

During 1899 Smith[1] devised a volumetric method based on a titration of the arsenious oxide in Paris green after all of the copper had been removed and the arsenic reduced to the "ous" condition. This method was a great improvement over the old ones in that one could make a determination of the total arsenious oxide in a single sample of Paris green in about forty-five minutes.

During September, 1900, the author[2] published a paper upon "The Adulteration and Analysis of Arsenical Insecticides" in which a comparison was made of the Smith method and two or three of the old methods mentioned above. It was shown by this study that the old methods based on the magnesium precipitation

[1] This Journal, **21**, 769.
[2] *Ibid.*, **22**, 568.

gave low results, while the Smith method always gave correct results, if a few simple precautions were taken that had not been mentioned by Smith in his original article.

In 1901, Avery and Beans[1] published a method for determining total arsenious oxide in Paris green. Since this method is the one that is to be critically studied, it will be given in full.

Method.—Sample the Paris green (as one would an ore for assaying) down to about 1 gram. Pulverize this small sample in an agate mortar and weigh out 0.2 to 0.3 gram in a beaker of, say, 300 cc. capacity. Add 25 cc. of water, and to the green suspended in the water add, with constant stirring, concentrated hydrochloric acid till solution is just effected. Six to twelve drops are usually sufficient. Now add to the acid solution sodium carbonate solution till a slight permanent precipitate is formed. Dissolve this precipitate by adding 2 to 3 grams of sodium potassium tartrate in solution. Now dilute to about 200 cc., add solid sodium bicarbonate and starch solution, and titrate with iodine in the usual way.

In a critical study that was made of this method in comparison with others, by the Association of Official Agricultural Chemists, it was shown by the author and other chemists that most excellent results were obtained when pure samples of Paris green were examined, but that when samples of greens containing considerable quantities of free arsenious oxide were examined, the method always gave low results. This was due to the fact that the free arsenious oxide was not dissolved by hydrochloric acid in the cold. Since any method that is to be used for determining total arsenious oxide in Paris green should include the free arsenious oxide, which is one of the most common adulterants, it at once became evident that the method would have to be modified to admit of its application in general work, especially in station control work. As this method, with pure Paris greens, is accurate as well as extremely short (only about five minutes being required for a single determination), it appeared to the author that any slight modification of it which would allow of its application to Paris greens containing free arsenious oxide, would be well worthy of some study. With this end in view, the following experimental work was carried out.

EXPERIMENTAL WORK.

Experiment 1.—It was at first thought the method might be modified in the following manner: Carry the manipulation down

[1] This Journal, **23**.

to the point where hydrochloric acid has been added, a drop at a time, to get the Paris green in solution. At this point all Paris green will be dissolved, while most of the free arsenious oxide will remain undissolved. Now add a slight excess of sodium carbonate and boil to get all arsenious oxide into solution, cool, acidify with hydrochloric acid, a drop at a time, add sodium bicarbonate until a faint precipitate is apparent, then sodium potassium tartrate, then an excess of sodium bicarbonate and after dilution titrate with iodine in the ordinary way.

Working in this way upon a Paris green that had been shown to contain 67.98 per cent. total arsenious oxide by the Smith method, of which 27.50 per cent. was free arsenious oxide, the following results were obtained: 66.55 per cent.; 67.50 per cent.; 67.15 per cent.; and 67.70 per cent. It at once became evident that, while this method sometimes gave practically correct results, the tendency was toward low results, so that it was not to be depended upon unless the factors that caused the variation could be discovered and controlled.

Since prolonged boiling of arseni*ous* compounds with alkalies is apt to cause the formation of arsen*ic* compounds, it was thought that the length of time of boiling the solution might cause the reduction in the amount of arsenious oxide found. To test this, definite weights of the Paris green were treated as above, using 1 gram of sodium carbonate for each determination, and the boiling was continued for varying lengths of time. The following results were obtained:

Time of boiling. Minutes.	Arsenious oxide. Per cent.
4	67.26
8	67.26
10	63.95
20	63.43
30	Decided reduction of the copper.

It appeared then, from the above table, that the longer the boiling was continued the lower the results, and that the low results were caused by the action of sodium carbonate on the Paris green, resulting in the reduction of the copper and consequent oxidation of part of the arsenious oxide.

Since only slightly low results were obtained when the green was boiled for from four to eight minutes with 1 gram of sodium carbonate, it was thought that by reducing the amount of the

sodium carbonate and only boiling from four to eight minutes, the error due to the action of the sodium carbonate upon the Paris green might be so reduced as to be negligible. Working upon this basis, the following results were obtained:

Time of boiling. Minutes.	Amount of sodium carbonate used in excess of that necessary to neutralize the hydrochloric acid.	Arsenious oxide found. Per cent.
7	7 drops of a saturated sodium carbonate solution.	67.39
7	4 drops of a saturated sodium carbonate solution.	67.44

Even in this case, with a minimum of sodium carbonate and a minimum time of boiling, low results were obtained and it was evident that the method was worthless.

Experiment 2.—An attempt was made to use sodium bicarbonate instead of sodium carbonate; the method in all its other details was the same as described in Experiment 1.

Working in this way upon the same Paris green, the following results were obtained where definite weights of the green were used; a definite quantity of sodium bicarbonate (10 grams) was added in each determination and the time of boiling was varied.

Time of boiling. Minutes.	Arsenious oxide. Per cent.	
5	67.44	(a few flakes of arsenious
10	67.96	oxide undissolved.)
10	67.96	
15	67.35	
20	66.92	
40	63.43	(decided reduction of copper.)

It appeared from the above table that five minutes' boiling was not sufficient to cause all of the free arsenious oxide to go into solution; that ten minutes' boiling gave theoretical results, while with fifteen, twenty and forty minutes' boiling the results were progressively lower, until at forty minutes a marked reduction of the copper and consequent oxidation of arsenious oxide were shown.

The ten-minute period of boiling with 10 grams of sodium bicarbonate was tried with various other Paris greens, but low results were obtained in so many cases that it was seen that the time of boiling must be altered for different samples, thus rendering the method valueless.

An attempt was made to reduce the amount of sodium bicarbonate and so get correct results, but it was found that unless the sodium bicarbonate was present in comparatively large quantities, the free arsenious oxide went into solution very slowly, so that a prolonged boiling was necessary, which always resulted in a slight reduction of the copper of the Paris green.

Experiment 3.—The only other way of applying the Avery-Beans method of analysis to Paris green containing free arsenious oxide that suggested itself to the author was to separate the undissolved, free arsenious oxide and the dissolved arsenious oxide and to determine them separately. To do this the following method of analysis was used: Sample the Paris green (as one would an ore for assaying) down to about 2 grams. Pulverize this small sample in a mortar and place from 0.3 to 0.4 gram in a beaker. Add about 25 cc. of water and, while constantly stirring, add concentrated hydrochloric acid, a drop at a time until all the Paris green is in solution and the free arsenious oxide remains as a residue. Filter and wash the residue. The arsenious oxide in the filtrate is determined in exactly the same manner as is given in the original Avery-Beans method. The filter and contents are dropped back into the beaker, which also receives the water used in washing the funnel. Five grams of sodium bicarbonate are added and the solution boiled until the arsenious oxide is completely dissolved (this takes from five to ten minutes). The resulting solution is cooled and acidified, using a drop of methyl orange to read the change. It is then made alkaline again with sodium bicarbonate, starch is added and the arsenious oxide titrated in the usual way with standard iodine. By this method the results given in the following table were obtained. There are also given the results obtained by the Smith method, which we know to be correct, and a determination of the free arsenious oxide by the sodium acetate extraction method and by the ten-day water extraction method.

	Soluble As_2O_3 sodium acetate extraction.	Soluble As_2O_3 10-day water extraction.	Total As_2O_3 Smith method.	Total As_2O_3 modified Avery-Beans method.
Sample No. 1...	7.25	8.75	58.98	59.17
" " 2...	13.50	14.90	61.71	61.68
" " 3...	26.00	28.00	67.60	67.42
" " 4...	7.18	8.19	59.86	59.87

It will thus be seen that by modifying the Avery-Beans method

as above, it can be applied to Paris green containing free arsenious oxide and will give results which are strictly comparable with the Smith method. While this modification increases the time of carrying out the analysis on a single sample from about five to twenty minutes, it still results in a method which is much shorter than any known by the author for this class of compounds.

Now that the above modification has been worked out, it appears so simple and obvious that the author almost feels reluctant to publish it. When it is taken into consideration, however, that the Avery-Beans method has been before the Association of Official Agricultural Chemists for two years and that, although its limitations were spoken of, no one suggested the above change; that the author has also worked with the method for about two years without previously thinking of the change and that finally Avery and Beans, the originators of the method, did not suggest the above simple modification so that it might be applied to Paris green adulterated with arsenious oxide, it seems that the results are worthy of publication, especially since a shorter time and fewer manipulations are involved than in any other method for determining arsenious oxides in Paris green at present known to the author.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 87.]

A MODIFICATION OF THE BABCOCK-BLASDALE VISCOSITY TEST FOR OLIVE OIL.

BY HERBERT ABRAHAM.

Received June 26, 1903.

ACCORDING to Blasdale, Prof. Rising was the first to suggest the possibility of using the factor representing the viscosity of the soap solution formed from a fixed amount of olive oil, saponified by a definite amount of potassium hydroxide, for detecting adulterated samples. At his suggestion Babcock, who had in 1886[1] examined a number of samples of butter and its principal adulterants, tested also a few of the most common fatty oils. His results show that butter gave the soap of lowest viscosity, and he also remarked that among the fatty oils, olive gave one of about the highest viscosity. The method was, at this time, used simply

[1] Reports N. Y. State Agricultural Experiment Station, 1886, p. 338; and 1887, p. 380.

for the examination of butter, and it was only in 1895 that Blasdale[1] applied it to olive oils. His paper contains the results obtained from a number of samples of pure and commercial olive oils, and also from a few oils which might be used as adulterants of olive oil. The figures obtained with different pure samples of olive oil varied considerably, but were always higher than those of the adulterated oils.

The method was considered especially promising for the detection of lard oil and as, at present, no good method is known by which the presence of the latter in olive oil can be determined with any degree of accuracy, its importance is obvious.

That this method has not come into more general use may be ascribed to the difficulty experienced in obtaining concordant results.

The writer has undertaken to study and, as far as possible, to mitigate or obviate the causes which led to the discrepancies in the method as hitherto carried out.

At first the method used by Blasdale[2] was strictly followed, but this was soon modified with respect to the means of determining the viscosity of the soap solution eventually obained. Doolittle's viscosimeter[3] was employed in the earlier tests, but the cost of this instrument has restricted its use to but a few laboratories. Moreover, for the present purpose there seems to be no theoretical advantage in measuring the viscosity by the torsion method, and no objection to the use of a viscosimeter which determines the rate of flow of the liquid through an aperture. In addition to being accurate, inexpensive, and easy of manipulation, it is important that the instrument used should be of such construction as to be readily kept at the desired temperature. Ostwald's viscosimeter[4] appears to meet these requirements more satisfactorily than any other with which the writer is familiar, and it was thought that a comparison of this with the Doolittle viscosimeter might yield results of value. The following were obtained on testing aqueous solutions of sucrose.

[1] This Journal, **17**, 937 (1895).

[2] Fifteen grams of oil are weighed in a saponification flask, and treated with 30 cc. of water containing exactly 7.5 grams potassium hydroxide, and 10 cc. of alcohol. This is heated on a water-bath until complete saponification has been effected. The resulting soap is washed into a large evaporating dish, heated until all the alcohol is expelled, and diluted to exactly 500 cc. at 15° C. The viscosity is determined by means of a torsion viscosimeter and calculated in terms of grams sugar per liter.

[3] This Journal, **15**, 173 (1893).

[4] Ostwald-Luther : "Physico-Chemische Messungen," 2nd edition (1893), p. 266.

Grams sugar per liter.	Doolittle's viscosimeter. I. Retardation at 26.6° C.	Differences.	II. Log. decrs. at 20° C.	Differences.	Ostwald's viscosimeter. III. Abs. viscosimeter at 20° C.	Differences.
0	6.7	..	255	..	100	..
100	7.1	0.4	295	40	132	32
200	7.5	0.4	345	50	186	54
300	8.0	0.5	410	65	306	120
400	8.9	0 9	500	90	455	149
500	11.0	2.1	670	170	712	257
600	14.5	3.5	...	...	1448	736
700	21.5	7.0	...	...	....	...
800	32.8	11.3	...	...	....	...
900	71.5	38.7	...	...	....	...

Column I gives the results expressed by the method employed by Doolittle, Column II by the method used by Babcock,[1] and Column III in terms of the absolute viscosity as will be used throughout the following work.

It will be noted that Columns I and III are obtained directly from the readings, while the results in Column II have been increased without rendering them more accurate, by obtaining the logarithmic decrements and then multiplying by 10,000. In spite of this, however, the ranges between the consecutive figures in Column III are greater than those in the other two columns. Ostwald's viscosimeter is, therefore, quite as delicate as Doolittle's. It costs about forty cents, whereas the Doolittle viscosimeter is sold for $65. Moreover, Ostwald's instrument requires for a test only about one-hundredth as much of the liquid, and, on account of its smaller size, it is easier to maintain at the desired temperature throughout the operation.

The changes which next suggested themselves were (1) the avoidance of transferring the soap from one vessel to another, and (2) the use of a smaller bulk of soap solution.

Both were effected by employing one-fifth the quantities of oil, potassium hydroxide,[2] and of alcohol used by Blasdale. This corresponds to a soap solution of 100 cc.

As the results of considerable study of the details of manipulation, it was found that the principal causes of variable results obtained by the method are (1) variations in the amount of

[1] Report N. Y. State Agricultural Experiment Station for 1886, p. 316; also *J. Anal. Chem.* (1887), **1**, 151.

[2] This amount was subsequently diminished slightly in order to obtain more concordant results.

caustic potash present in excess; (2) incomplete expulsion of the alcohol used in saponification; (3) absorption of carbon dioxide by the excess of alkali, during the expulsion of the alcohol; (4) varying the temperature at which the actual viscosity is determined; (5) varying the dilution of the soap solution.

Each of these points was studied separately with a view of finding the best conditions of manipulation.

Varying the Amount of Potassium Hydroxide Used.—It was found that the viscosity of the soap solutions increased rapidly with the amount of potassium hydroxide present in excess of that

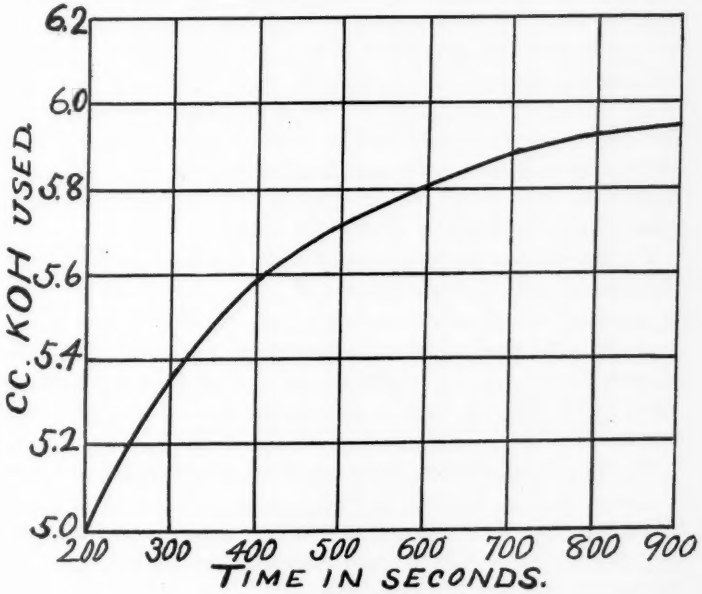


Fig. 1.

required for saponification. Thus, with an olive oil, saponified with 5 cc.[1] potassium hydroxide, the average time of flow was 200 seconds; with 5.2 cc., 253 seconds; with 5.4 cc., 310 seconds; with 5.6 cc., 412 seconds; with 5.8 cc., 568 seconds; with 6 cc., the soap was to viscous to test to any degree of accuracy.

These results are plotted in the form of a curve (Fig. 1). It is evident from these experiments that relatively small variations

[1] One cc. containing 1/4 gram exactly.

in the amount of free alkali present cause large changes in the viscosity of the solution. Even the variations due to the differences in the Koettstorfer figure of different samples may seriously affect the results. It is much better, therefore, instead of using a *fixed amount* of alkali in each case, to determine the alkali required for the saponification of each sample, and then vary the amount of alkali taken so that the soap solution to be tested will always contain a *fixed excess* of potassium hydroxide.

Expelling the Alcohol Completely with "Ordinary Air."—The same oil saponified with 4.80 cc. potassium hydroxide (2.50 cc. in excess of that required for saponification) etc., and the alcohol expelled completely by a current of air passed over the surface of the liquid, gave an average time of flow of 148 seconds.

Expelling the Alcohol Completely with "Ordinary Air" as above, Followed by Passing in Carbon Dioxide (Converting all the Caustic into Carbonate).—The same oil under this treatment gave an increase of 93 seconds in the time of flow, while the soap solution of another oil, whose original time of flow was 137.2 seconds, was increased by nearly 23.8 seconds.

These and other irregularities led to the conclusion that the use of carbon dioxide is unsatisfactory.

Expelling the Alcohol Completely with Air Free from Carbon Dioxide.—The same oil saponified as above, and having a stream of pure air passed over its surface for half an hour while being heated on a water-bath, gave an average time of flow of 151.6 seconds.

This led to the adoption of air free from carbon dioxide.

Length of Time Required to Expel the Alcohol.—Saponification as above with a Kroonig valve in fifteen minutes, the viscosity being determined directly without expelling the alcohol, gave an average time of flow of 143 seconds.

Another portion saponified in fifteen minutes, with air free from carbon dioxide passed through for fifteen minutes, gave an average time of flow of 150.4 seconds.

A third portion saponified as above, air free from carbon dioxide being passed in for ten minutes, gave an average time of flow of 15.2 seconds.

Ten minutes was, therefore, considered sufficient for the removal of the alcohol.

Varying the Temperature.—Saponified with 4.80 cc. potassium hydroxide, etc., in fifteen minutes, air free from carbon dioxide being then passed in for ten minutes. When the soap solution was tested at 15° C., the time of flow was 205.3 seconds; at 16° C., 196.0 seconds; at 17° C., 185.0 seconds; at 18° C., 172.7 seconds; at 19° C., 161.3 seconds; at 20° C., 150.4 seconds; at 21° C., 142.0 seconds; at 22° C., 134.3 seconds; at 23° C., 127.0 seconds; at 24° C., 120.0 seconds; at 25° C., 114.0 seconds.

The results are plotted in a curve (Fig. 2).

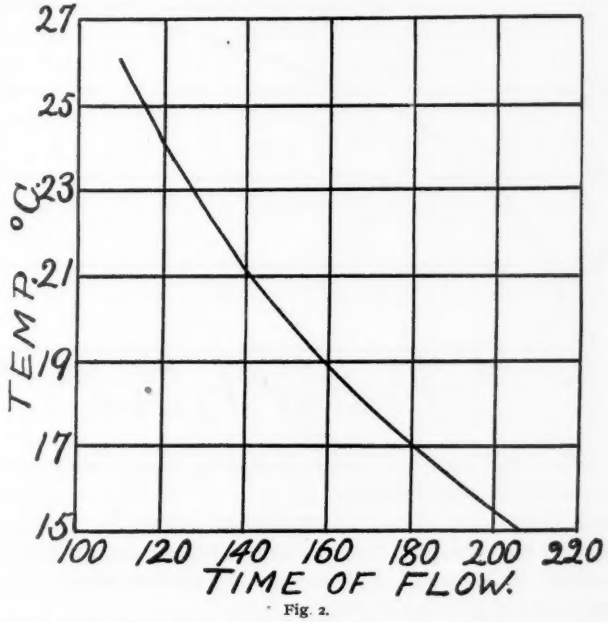


Fig. 2.

Varying the Dilution of the Soap Solution.—The average time of flow of a certain soap solution was 161 seconds; the same, three-quarters strength, was 120 seconds; one-half strength, 105 seconds; one-quarter strength, 98 seconds; for water alone, 95 seconds. The results are plotted in Fig. 3.

In order to avoid or minimize any variations arising from the above conditions, and to obtain a solution of such a viscosity as to permit of convenient and accurate measurement, the following details should be observed:

(1) In every case add exactly 2.5 cc. of potassium hydroxide (0.25 gram per cubic centimeter) in excess of that required for saponification. This amount is desirable as it gives a comparatively low viscosity, offering the following advantages: (*a*) It takes less time to flow, reducing the total time of the method; (*b*) the soap dissolves more easily; (*c*) the results are more uniform and are just as accurate.

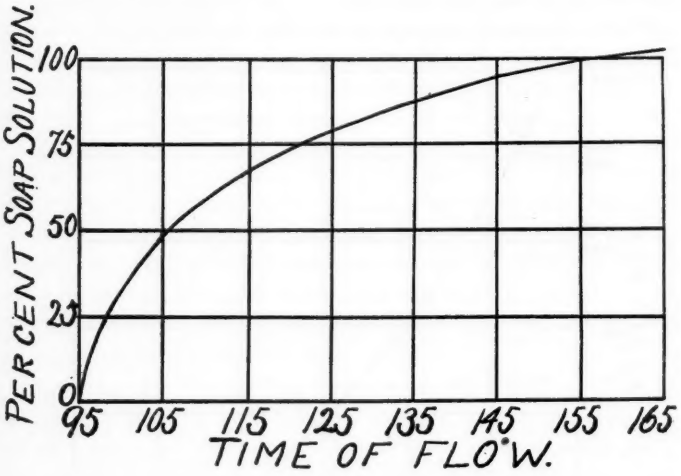


Fig. 3.

(2) Two cc. of alcohol are chosen as being the minimum amount to secure rapid saponification.

(3) The alcohol should be expelled completely by means of a stream of air, free from carbon dioxide, passed through the flask for about ten minutes. This secures the greatest accuracy combined with the greatest rapidity.

(4) The soap should be diluted to 100 cc. in conformity with the above conditions.

(5) The viscosity should be determined at *exactly* 20° C.

THE METHOD AS FINALLY ADOPTED.

I. Apparatus.—(*a*) 100 cc. flasks accurately calibrated and thoroughly cleansed and dried; (*b*) a "water-suction apparatus" capable of raising a column of mercury at least 300 mm.; (*c*) a 5 cc. measuring pipette, graduated accurately to $^1/_{20}$ cc. for measuring out the potassium hydroxide solution. The end of this

pipette should be drawn out into a thin-walled capillary so as to decrease the size of the drops and thus render the delivery more accurate. The diameter of the capillary should be such that 60 to 65 drops of the potassium hydroxide solution are delivered per cubic centimeter;[1] (*d*) a stopper with a Kroonig valve to fit the 100 cc. flasks, used while saponifying. This permits any vapors to escape, but does not allow air to enter the flask, thus avoiding contamination by carbon dioxide; (*e*) a ring-stand carrying a water-bath and U-tubes to remove carbon dioxide from the air used; (*f*) an Ostwald viscosimeter and accessories.

II. Reagents—(*a*) A solutionof potassium hydroxide containing *exactly* 0.25 gram per cubic centimeter, made up accurately by titration; (*b*) alcohol practically free from impurities, used in titrating. This should be tested for acidity and neutralized, if necessary; (*c*) a solution of phenolphthaleïn, 1 gram per liter in pure alcohol; (*d*) ether for washing out the viscosimeter, pipettes, etc.; (*e*) standard hydrochloric acid approximately N/5.

III. Determination.—Weigh out two portions of exactly 3 grams of the oil into 100 cc. flasks, care being taken not to introduce any on the necks of the flasks.

Determination of the Amount of Potassium Hydroxide Required for Saponification.—To one portion add 5 cc. potassium hydroxide and 2 cc. alcohol from their respective pipettes. Adjust the seal and heat on the water-bath for from ten to fifteen minutes, when the saponification should have taken place. Rinse the soap into a beaker with about 100 cc. pure alcohol, add 10 to 12 drops phenolphthaleïn, and titrate with hydrochloric acid. Calculate the amount of potassium hydroxide to be added next time in order that there shall be 2.5 cc. in excess of that required for saponification.

Preparing the Soap Solution.—To the second portion of oil, add the calculated amount of potassium hydroxide, and 2 cc. alcohol. Adjust the seal and saponify on the water-bath. The time required for saponification may be materially reduced by occasionally twirling the contents of the flask. If thus agitated at intervals, it rarely takes longer than ten minutes. After saponification, the seal is replaced by a stopper carrying two tubes, a short one and

[1] The pipette used by the writer was calibrated by weighing the water which it delivered at 20° C.; when 5 cc. were delivered altogether the accuracy was $\pm$ $^1/_{100}$ cc., while the greatest error for any individual cubic centimeter was $^1/_{70}$ cc.

a long one, drawn out so as to come about 5 to 10 mm. above the surface of the liquid. The lower end of the longer tube is curved upwards so as to present the mechanical carrying off of the liquid. The other end of this tube is connected with the suction, while the shorter tube is connected with the absorption train. By placing the finger over the entrance to the last U-tube, a partial vacuum is created in the flask, and the evaporation of water and alcohol is accelerated, as is seen by the frothing of the soap. The finger is removed, and the operation repeated once or twice at intervals. The evaporation should not be carried so far as to remove the water present, else the soap will solidify and take an inconveniently long time for its subsequent solution. It will suffice to take the soap down to the consistency of molasses (which requires five to ten minutes). Without allowing it to cool, the flask is filled about half full of boiling water. Upon rotating, the soap should go into solution in a minute or two. The flask is now immersed in a stream of cold water until it attains about the temperature of the room, when it is diluted to the mark with cold, distilled water and mixed well by shaking.

Finding the Viscosity.—The viscosimeter should be cleaned by attaching it to suction and running first alcohol and then ether through it; it is then immersed in a cylinder filled with water kept *exactly* at 20° C.

Great care must be exercised on introducing the 3 cc. of soap solution into the viscosimeter, and, on sucking it up the capillary (which must be done very slowly), because if it once becomes frothy, it will be almost impossible to secure a satisfactory reading. With a little practice in manipulation, however, the soap can be maintained free from enclosed bubbles during the entire operation. The first reading is usually rejected so as to give the liquid a chance to assume the temperature of the surrounding water-jacket. Five or more closely agreeing readings should be averaged to obtain the time of flow. The readings should agree within two seconds. The instrument is first calibrated by using pure, distilled water which should take in the neighborhood of 100 seconds to flow through. Since the instruments are made of capillary tubes of different diameters, one should be selected which takes about 100 seconds with water—this being most satisfactory for the method.

The "absolute viscosity" is calculated by means of the following formula:

$$v_1 = \left(\frac{s_1}{t}\right) t_1,$$

where t_1 = the time of flow,

s_1 = the specific gravity of the liquid under consideration,

and t = the time of flow of water under like conditions.

The specific gravities of the soap solutions of all the principal oils, as based on a large number of determinations, were found to approximate 1.07 (within ± 0.005), so that this figure may be substituted in place of s_1 in the above expression. An extreme error of 0.005, due to this assumption, will merely affect v_1 by 0.5 to 0.7.

The formula, therefore, reduces to

$$v_1 = kt_1,$$

where k is a constant for the particular apparatus employed. The value of v_1 for pure, fresh olive oil of good quality is usually 165-185, for most other oils it is about 125-135.

In general, it is advisable to determine the viscosity of the soap solution while fresh, as it has been found that after standing several days the viscosity is sometimes increased and sometimes decreased.

In the hands of the writer, the time required for a determination by the present method is less than half that required by the method as described by Blasdale.

In conjunction with Dr. H. C. Sherman, at whose suggestion this investigation was undertaken, the modified method has been applied to a number of samples of olive, lard, and other fatty oils, in comparison with the "constants" by means of which such oils are usually judged. The results of this study will be given in a subsequent paper.

QUANTITATIVE LABORATORY,
June, 1903.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 88.]

THE VISCOSITY OF THE SOAP SOLUTION AS A FACTOR IN OIL ANALYSIS.

BY H. C. SHERMAN AND HERBERT ABRAHAM.

Received June 26, 1903.

AS PART of a comparative study, undertaken in this laboratory, of some of the so-called analytical constants, we have determined

the viscosities of solutions of the potassium soaps of several vegetable and a few animal oils. The method of making this viscosity test" and the principal conditions which influence the results have been fully described by one of us.[1] In the present paper, we give the figures obtained by the method as finally adopted, and compare them with some of the more commonly determined constants.

The specific gravities and iodine absorption (Hübl) figures were determined as in previous investigations.[2] The figure here called "Specific Maumené" is the rise of temperature produced on mixing 10 cc. of sulphuric acid with 50 grams of the oil, the result expressed in percentage of the rise shown by 50 grams of water under the same conditions.[3] The reaction was carried out in small, jacketed beakers, ordinary "C. P. concentrated" acid being used, except in cases where the reaction became too violent, when acid of about 89 per cent. was substituted, as noted below.

All of the olive oils tested were purchased from presumably reliable dealers in New York City and are believed to be pure, though some are cheap oils of rather poor quality. With the exception of No. 18, all of the samples of lard oil, cottonseed and maize, and the first sample of linseed were sent to us by the makers as pure typical specimens. The remaining samples were purchased from responsible dealers and are believed to be pure. The dates given in the table indicate the years in which the samples were obtained by us.

The results obtained are shown in the following table:

VISCOSITY FIGURES AND OTHER CONSTANTS OF SOME FATTY OILS.

No.	Description of oil.	Sp. gr. 15.5°.	Hübl figure.	Specific Maumené.	Viscosity figure.
1	Olive, "Lucca," 1903	0.9144	79.7	88	168.4
2	Olive, "Marseille," 1903.....	0.9152	82.3	91	168.0
3	Olive, "Niece," 1903	0.9156	81.5	88	174.6
4	Olive, "Bordeaux," 1903.....	0.9158	81.0	88	185.5
5	Olive, "Bordeaux," 1903.....	0.9160	81.6	88	185.7
6	Olive, "California," 1903	0.9160	86.0	93	180.0
7	Olive, "Bordeaux," 1903.....	0.9162	80.6	87	174.4
8	Olive, "Marseille," 1903.....	0.9162	83.9	97	145.8
9	Olive, "Lucca," 1901	0.9165	80.5	..	165.8
10	Olive, "Bordeaux," 1903.....	0.9165	84.5	100	151.9
11	Olive, unknown origin, 1899 ..	0.9170	84.5	100	153.7
12	Olive, unknown origin, 1903 ..	0.9171	81.5	89	168.0

[1] See the preceding paper.
[2] This Journal, **23**, 168.
[3] This Journal, **24**, 266–273.

VISCOSITY FIGURES AND OTHER CONSTANTS OF SOME FATTY OILS.—(*Continued*).

No.	Description of oil.	Sp. gr. 15.5°.	Hübl figure.	Specific Maumené.	Viscosity figure.
13	Olive, unknown origin, 1901 ..	0.9177	86.1	106	157.9
14	Lard oil, first quality, 1903	0.9165	72.1	92	135.0
15	Lard oil, second quality, 1903..	0.9181	74.2	99	133.1
16	Lard oil, third quality, 1903 ...	0.9187	63.9	79	126.9
17	Lard oil, best commercial, 1900	0.917	73.3	106	122.9
18	Lard oil, for lubricating, 1899 .	0.919	72.5	88	128.1
19	Almond, commercial, 1899	0.919	98.1	114	167.8
20	Arachis, commercial peanut, 1899	0.917	105.9	176	126.6
21	Castor, crystal, 1899	0.964	86.9	94	126.6
22	Cotton, prime summer yellow, 1900	0.920	102.8	161	127.9
23	Cotton, choice summer white, 1900	0.923	105.2	171	126.6
24	Cotton, old sample	0.926	103.3	197[1]	126.6
25	Rape, commercial, 1901	0.920	107.4	144[1]	125.6
26	Rape, unknown origin.....	0.920	108.6	...	125.7
27	Rape, unknown origin, old....	0.926	99.3	...	124.7
28	Blown rape, commercial, 1901 .	0.974	56.6	...	123.2
29	Sesame, commercial, 1899	0.924	105.3	158	139.2
30	Maize, from glucose works, 1900	0.924	117.2	174	126.6
31	Poppy, unknown origin	0.925	125.3	212[1]	123.9
32	Linseed, from Dakota seed, 1900	0.934	180.1	300[1]	126.6
33	Linseed, commercial, 1898.....	0.938	177.1	298[1]	126.6

COMPARISON OF VISCOSITY FIGURE WITH OTHER CONSTANTS.

The olive oils in the table are arranged in the order of their specific gravities and it will be seen that, with few exceptions, the increasing specific gravity is accompanied by increasing iodine absorption of Maumené figures, while the viscosity figure, as a rule, decreases. This may be shown by averaging separately the samples falling in the first and second halves as given in the table. The results are:

	Specific gravity.	Hübl figure.	Specific Maumené.	Viscosity.
Average, Nos. 1-7..	0.9156	81.8	89	176.7
Average, Nos. 8–13.	0.9168	83.5	98	157.2

The first group gives average figures which would indicate purity and high quality, and here the viscosity figures are high. The second group gives results which would be taken as indicating a lower quality of oil, and here the viscosity figures average much lower. It is interesting to note in this connection that five of the

[1] Determined by the use of acid of about 89 per cent.

seven samples in the first group were commercially rated as extra high grade, and that four of the six samples in the second group were cheap oils.

Comparing samples Nos. 14, 15 and 16, lard oils of first, second and third quality from the same maker, it appears that here also the viscosity figure decreases with the quality of the oil, though the differences are too small to be of much significance.

Comparing olive oils with other oils, the only one of the latter examined by us which equals olive in its viscosity figure, is almond oil with a figure of 167.8. Next below comes sesame with a figure of 139.2. Blasdale[1] has already stated that almond equals, and sesame approaches, olive oil in this respect. We have, however, been unable to confirm his statement that rape oil gives a soap solution of as high viscosity as that of olive oil. The high result obtained by Blasdale may be due to the fact that he used a fixed amount, instead of a fixed excess, of alkali for saponification. This procedure would, of course, leave a larger amount of uncombined alkali in the case of rape than with the other oils, and this larger excess of alkali would increase the viscosity of the soap solution. We have not examined mustard-seed oil, which according to Blasdale yields a soap solution of very high viscosity.

All of the samples examined by us, other than olive, almond and sesame oil, showed viscosity figures between 122 and 135. It seems remarkable that this figure should show such slight variations between oils differing so markedly in other properties as, for example, lard, linseed and castor oils.

From the results obtained with castor and with blown rape-seed oils, it is evident that the viscosity of the soap solution is independent of the viscosity of the oil itself.

Our results fully confirm the conclusion reached by Blasdale that the adulteration of olive oil with any other oil likely to be used for the purpose would result in a lowering of the viscosity figure. The following experiments were designed to determine whether the viscosity figure actually found in such a mixture would agree with that calculated from the constituents. Soap solutions of lard, cottonseed, and peanut oils were mixed in different proportions with those of olive oil and the viscosities determined with the following results:

[1] This Journal, 17, 940.

MIXTURES OF SOAP SOLUTIONS OF OLIVE AND OTHER OILS.

Nature of soap solution.	Viscosity figure. Found.	Calculated.
Olive oil	168.4	....
Lard oil	128.1	....
3/4 olive, 1/4 lard oil	158.6	158.4
1/2 olive, 1/2 lard oil	147.6	148.2
1/4 olive, 3/4 lard oil	137.8	138.2
Peanut (arachis) oil	126.6	....
3/4 olive, 1/4 peanut oil	143.6	158.0
1/2 olive, 1/2 peanut oil	134.2	147.5
1/4 olive, 3/4 peanut oil	129.0	137.1
Cottonseed oil	127.9	....
9/10 olive, 1/10 cottonseed oil	152.0	164.4
3/4 olive, 1/4 cottonseed oil	142.6	158.3
1/2 olive, 1/2 cottonseed oil	132.1	148.2

From this table it appears that mixtures of olive and lard oils give practically the calculated results, while the viscosities of mixtures of olive with cottonseed or peanut oils are lower than would be calculated from the viscosities and proportions of the oils in the mixture. Hence the adulteration of olive with cottonseed or peanut oil produces a greater change in the viscosity figure than that which would have been predicted.

A somewhat similar, but more striking result was obtained from the examination of mixtures of soap solutions of pure fatty acids. Such mixtures also give viscosities lower than would be calculated. Three grams of lauric acid, treated in the same manner as described for fatty oils, gave a viscosity figure of 126.6, oleic acid gave a figure of 239.7, while stearic acid yielded a soap solution too viscous to be tested at ordinary temperatures. Yet large proportions of the oleate or stearate solution could be added to the laurate solution without appreciably increasing its viscosity.

INFLUENCE OF ATMOSPHERIC OXIDATION.

In view of the fact that even the so-called non-drying oils may undergo sufficient oxidation from simple exposure to air to affect seriously the "constants" usually determined in oil analysis,[1] it is of some importance to determine the effect of such oxidation upon the viscosity figure. Speaking generally, it appears that the effect of sufficiently prolonged exposure is to cause olive and almond oils to lose their characteristic high viscosity figures while those oils whose figures are lower are but little affected. A sample of olive oil exposed in an uncorked bottle for several months

[1] This Journal, 2 , 711.

showed a loss of 7 units in the Hübl figure and of 25 units in the viscosity figure. An almond oil, similarly exposed for a longer time, decreased from 98.1 to 84.6 in the Hübl figure and from 167.8 to 123.8 in the viscosity figure. On the other hand, a sample of lard oil exposed until the Hübl figure fell from 73.3 to 66.7 showed no appreciable change in the viscosity figure; and in several samples of cottonseed, maize and linseed oils, in which atmospheric oxidation had caused losses of 10 to 40 units in the Hübl figures, the decrease in the viscosity figure was in no case greater than 4 units.

SUMMARY.

Olive and almond oils yield soap solutions of considerably greater viscosity than those obtained from the other more common fatty oils.

This "viscosity figure" is apparently higher in the better than in the poorer grades of olive oil.

The lowering of the viscosity figure by admixture of other oils furnishes an additional method for the detection of adulteration in olive and almond oils. As suggested by Blasdale, it will be especially useful for the detection of lard oil for which we have no specific test. The characteristic high viscosity figure of olive or of almond oil may be largely lost on sufficiently long exposure of the oil to air at ordinary temperature.

While the reason for the high figures shown by olive and almond oils cannot be stated, it appears probable that the explanation is to be found in the quantitative relations of the fatty acids present, rather than in the presence of any peculiar constituent, and that interesting results might be obtained from a study of the viscosities of the soap solutions of pure fatty acids and their mixtures.

QUANTITATIVE LABORATORY,
June, 1903.

[CONTRIBUTION FROM THE DEPARTMENT OF FOOD AND DRUG INSPECTION OF THE MASSACHUSETTS STATE BOARD OF HEALTH.]

THE DETERMINATION OF COMMERCIAL GLUCOSE IN MOLASSES, SYRUPS, AND HONEY.

BY ALBERT E. LEACH.

Received May 28, 1903.

THE importance of a ready method for the determination of so common an adulterant as commercial glucose is obvious. Several

of the states have in their food laws a provision requiring that so-called "compound" foods (such as molasses containing commercial glucose), to be legally sold, must have formulas setting forth the names and percentages of their ingredients. In such cases it becomes virtually a necessity for the analyst to be able to verify, within certain limits, such formulas and thus guard against fraudulent and misleading statements thereon.

Unfortunately, from the variability in composition of commercial glucose, there can obviously be no accurate method for its determination, especially in complex, saccharine products in which one is likely to find it, and which themselves contain components common to glucose.

In enforcing the food laws conservatively, a formula on a package expressing the name and percentage of ingredients in the food contained therein is not condemned, because it differs by a few per cent. only from the analyst's findings, nor should the presence of a mere trace of an adulterant, which may be accidental, serve as a basis for a complaint in court. It is only when substantial deviations from a manufacturer's formula are found, or the presence of enough of the adulterant is evident to make it an object for fraudulent use, that the analyst should condemn it. In cases like these, an approximate method must be used, but preferably one, the adaptability of which to the purpose in hand has been well tested by long trial.

In molasses, syrups, honey, and similar preparation wherein commercial glucose is present as an adulterant, it has been the practice of the writer for upwards of ten years in the prosecution of such cases under the food laws of Massachusetts to calculate the approximate amount of commercial glucose present by assuming 175 as the direct polarization of a normal weight of the glucose, 26.048 grams, made up to 100 cc. and polarized in a 200 mm. tube. From this was naturally developed the formula which was long afterwards included by the writer in the methods outlined by him as an associate referee for the analysis of saccharine products, and later incorporated in the provisional food methods of the Association of Official Agricultural Chemists,[1] as follows:

$$G = \frac{(a - S)\ 100}{175},$$

where G = per cent. of commercial glucose in the sample,

[1] Bureau of Chemistry, Bulletin 65, p. 48.

a = direct polarization of sample, and S = per cent. of cane-sugar as calculated from direct and invert polarization according to Clerget. This method and formula have been severely criticised by Mr. Edward Gudeman,[1] who regards the use of a single assumed factor as unwarranted, and one object of the present paper is to reply to his criticism and to show how satisfactorily the method has proved in practice. The formula applies more particularly to molasses and maple-syrup, as stated in the provisional methods. For honey, the same factor, 175, is used, but more accurate results are obtainable by dividing the polarization of the sample at 87° by this factor.

When asked in court, as one is sure to be in a contested case, the amount of commercial glucose in the sample, it is convenient to reply that *at least* such and such an amount must necessarily be present. By assuming in the above formula the highest figure that is apt to be found as the direct polarization of commercial glucose (175), it is obvious that the resulting value for S is the lowest or minimum one, thus giving the benefit of any doubt to the defendant. In other words, it is perfectly safe to allege that amount of glucose.

Realizing the uncertain composition of commercial glucose due to variations in amount of dextrose, maltose, dextrine and water present therein, the above method of calculation was long regarded by the writer as of doubtful value on theoretical grounds, and was not published for several years after being used. Continued opportunities were furnished, however, for comparison of the results thus calculated with actual conditions prevailing, such for example as occasional recipes furnished by defendants in court showing how the products were mixed, and one could hardly fail to be impressed by the striking and almost invariable similarity in results. Longer experience produced greater confidence, and it was thought best to examine a number of samples of commercial glucose obtained in a variety of ways from confectioners, mixers of compound honey and molasses, and jelly and jam manufacturers, with a view to ascertain the grades actually used by them and hence best suited for their purpose. It was found that considerable uniformity prevailed in the character of the glucose employed for different uses, especially as regards polarization. Thus seven

[1] Proceedings of 19th Annual Convention of the Association of Official Agricultural Chemists, Bur. of Chem., Bull. 73, p. 65.

samples, obtained in 1893, 1898 and 1901 from as many different manufacturers of compound molasses and honey or from dealers supplying them, polarized as follows:[1] 173°, 171°, 176°, 175°, 178°, 168° and 177°, the average being 174°. The writer's experience is not in accord with Mr. Gudeman's, who states that he has never known the manufacturer of glucose to furnish special or uniform grades for special purposes. In this connection the following is in point from the letter of a kind friend who obtained, through a broker, samples of glucose for analysis and who quotes from the broker's letter: "I am sending you two samples of glucose from the factory with the following advice: *42° Bé. is the grade used for syrup and honey, the XXXXX is the grade used for chewing-gum.*" The latter grade was found to polarize at 184.6°.

Another letter from a molasses mixer, who labels his product correctly under the law, runs as follows: "*Only one kind of glucose* is used in this kind of mixture, a sample of which we send you, called in the trade mixing or "M" glucose; the gravity we believe is somewhere about 42° Bé."

The molasses mixer naturally prefers the grade of glucose which, by its consistency, is best adapted without further treatment for mixture with his product. If it is too heavy in body, it must first be watered, and again if too thin it is equally unfit for direct use. Commercial glucose of 42° Bé. in density is admirably suited to his purpose, and this is the grade that more often polarizes from 170° to 175°. A number of samples obtained from confectioners and makers of compound jellies and jams were found to polarize from 150° to 157°.

Out of eleven samples of commercial glucose used for a variety of purposes in food and obtained from manufacturers of these foods, but one sample was found to polarize above 178° (the "XXXXX" brand above referred to), and none below 150°. Doubtless wider variations may possibly occur in commercial glucose of different densities as found on the market, but the point made here is that only such grades as are adapted for the particu-

[1] Figures being expressed in terms of 26.048 grams glucose made up to 100 cc. with water and polarized in a 200 mm. tube on the cane-sugar scale of the S. & H. instrument. It should be noted that in polarizing glucose, or molasses and syrups adulterated therewith, a 100 mm. tube should be used and the necessary correction applied, in order to bring the high reading within the limits of the scale. For exact data as to clarification of sample and other precautions, the reader is referred to Bull. 65, Bureau of Chemistry, p. 47.

lar purpose in hand are used by the food manufacturer, and these come within certain particular limits.

Mr. Gudeman's deductions regarding the composition and variations of glucose show his familiarity with its manufacture, but he makes no mention of the effect of maltose as one of the important reducing sugars present, though he apparently makes allowance for it in a process which he suggests as an alternative to the provisional method. In this process he estimates the reducing sugars before and after inversion, and again after hydrolyzing with malt extract, calculating by difference the dextrose resulting from the hydrolysis of the non-reducing substances. In making the latter calculation, he assumes a factor which can be true only of a fixed proportion of maltose to dextrine, a condition which cannot, of course, be depended on. Another source of error in Gudeman's method lies in the fact that his results are expressed in percentage of dry substance, leaving one in the dark as to the actual amount of glucose present as an adulterant, unless one assumes also a definite percentage of water in the glucose. A determination of dry grape-sugar or dextrose in molasses or honey is of no importance whatever to the enforcer of the food law.

Mr. Gudeman seeks to prove the unreliability of the provisional method by applying it to various hypothetical mixtures of grape-, cane- and invert-sugar, for which the method never was intended and could not, under any possible conditions, be used. The provisional method applies solely to molasses and syrups as found on the market, and to the commercial glucose used as an adulterant. No ambiguity need attend the use of the term commercial glucose in this country. The product has too important a place in trade not to be a pretty well understood article. By it is not meant a mere haphazard mixture of dextrose, maltose and dextrine, but a well-defined series of graded products of varying density, depending on the degree of conversion, but which, as the result of long experience in manufacture, are fairly uniform, so that the product of a given grade or density has a polarization varying between narrow limits. While the confectioner from his multiplicity of products can use various grades, the honey and molasses mixer is limited to the use of a special grade best suited to his use.

In carrying out the provisional method, commercial glucose is considered as just as much of an entity as milk, for example. To cite a parallel case, it has long been a successful practice for the

food analyst to approximately calculate the amount of added water in milk by using an assumed constant for a factor, as for instance, the per cent. of solids not fat or total solids, in spite of the well-known wide variation in the normal constituents in milk. It is equally legitimate to adopt a constant for calculation of commercial glucose, based on such a uniform factor as the polarization seems to be in such cases.

Not the least of the advantages of the method is its simplicity, requiring only a direct and invert reading of the sample, which must be done in any event before deciding on the presence of commercial glucose. The method has never been claimed to be exact, but continued experience shows it to yield results much nearer the truth than was at first supposed possible.

Molasses, table syrup, and honey, put up in packages having incorrect formulas thereon, are included in the lists of adulterated brands, which, under the law, the Massachusetts Board of Health is obliged to publish monthly. The calculation of glucose in these cases is always based on the use of 175 as a factor, and experience has shown that manufacturers who doubt the findings of the Board are not slow to challenge its results.

Finally, the method has never been discredited, after long usage in the Massachusetts courts, where, of all places, in closely contested cases it is naturally subject to any criticism that may reasonably be brought against it.

PURIFICATION AND ESTIMATION OF IODINE.[1]

By Abraham Gross.

Received July 7, 1903.

In view of the importance of iodine in the arts and of the apparent difficulty in obtaining it absolutely pure, a discussion of this subject does not appear untimely and may prove of some value. Very few methods have been published in the direction of iodine purification and but one finds favorable mention. This is the method used by Stas in his researches on the atomic weight of iodine, and consists in dissolving iodine in a solution of potassium iodide, precipitating the iodine with water, drying over calcium nitrate, and subliming the dried mass. This method is criticized

[1] Read before the Pittsburg Section, June 18, 1903.

by Lean and Whatmough,[1] who state that pure iodine can be obtained by heating cuprous iodide in dried air at 240° C. when the iodine is liberated.

Other investigations on this subject have been made by C. Meineke[2] and Z. Musset.[3] With a desire to obtain a reliable method for purifying iodine it was considered advisable to test the efficacy of the Stas method, and to compare the purity of the iodine thus produced with that obtained by other methods which suggested themselves at the time.

Accordingly, the following methods were tried: (1) The Stas method; (2) washing iodine with water, drying a portion over sulphuric acid, another portion over calcium nitrate and a third portion over calcium chloride; (3) mixing iodine with potassium iodide and drying over sulphuric acid.

Each of the above was then sublimed three times after drying.

The first method was carried out according to the directions of Stas, who states that to dissolve four kilos of iodine a solution of 1 kilogram of potassium iodide in 1 kilogram of water was required. These proportions were found inadequate, for, after standing some time with frequent shaking, a considerable portion of the iodine remained undissolved.

Several additions of potassium iodide and water were made, until complete solution was effected. This was accomplished when the proportions were 4 of iodine to 2 of potassium iodide and 2 of water.

The solution of iodine was then poured into water and allowed to stand until all of the iodine was precipitated. The supernatant fluid was poured off and the iodine washed with water until free from potassium iodide. It was then brought upon a filter, with sand as a filtering medium, and the water withdrawn by suction. The iodine was then transferred to a shallow dish and dried over calcium nitrate, which was replaced as soon as affected by the moisture. The drying continued twelve days. The dried sample was then sublimed three times by a process which will be described later.

In the next three methods, the iodine was washed with water fifteen times, and, after as much water as possible had been withdrawn by suction, was divided into three portions and dried, as

[1] *J. Chem. Soc.* (London), 1899.
[2] *Chem. Ztg.*, **16**, 1219.
[3] *Ztschr. anal. Chem.*, 1891, p. 45.

previously mentioned, over sulphuric acid, calcium nitrate and calcium chloride respectively.

In conducting this experiment, two other points were in view: (1) To determine the best drying agent; (2) to ascertain whether any chlorine would be set free and absorbed by the iodine when the sample was dried over calcium chloride.

It may be mentioned here that the calcium nitrate and sulphuric acid were equally efficient as drying agents, but the inconvenience of constantly changing the calcium nitrate rendered it less desirable. Each of these samples was then sublimed three times.

The fifth sample was prepared by mixing iodine with pure potassium iodide, drying over sulphuric acid and subliming three times. The iodine obtained by this method was discarded, as a white residue remained after each sublimation. Apparently the potassium iodide was carried over with the iodine vapor.

PROCESS OF SUBLIMATION.

The iodine prepared by the methods previously described was placed in a piece of combustion tubing slightly inclined and resting on a support. Following the iodine was a plug of ignited asbestos to prevent the heated iodine from running down the tube. The lower end of the tube was connected to two tubes containing phosphoric anhydride and one containing calcium chloride. In this manner the air drawn through was perfectly dry. The upper end was covered by a bottle fitted to a rubber stopper to catch any vapor not previously condensed.

Through the stopper passed a glass tube which connected with an empty jar as a precautionary measure and in turn with a cylinder containing water and with the suction-pump. The suction was regulated by the bubbles produced in the cylinder. To prevent any accident from too sudden heating, a piece of iron pipe was placed over that part of the tube containing the asbestos and iodine and extending beyond for about 4 inches. This was protected from the glass by asbestos. A gentle heat was used and enough suction applied to condense the vapor sufficiently far away from the pipe to prevent any liquefaction of the sublimed crystals.

The succeeding two sublimations were conducted in precisely the same manner.

The following method proved itself highly satisfactory in the

determination of the purity of iodine. About 2 grams of the iodine were placed in a flask, 40 cc. of water, and about 4 grams of shot-zinc added. The flask was then shaken and allowed to stand with stopper inserted until the fluid was colorless. When all the iodine was taken up by the zinc, the solution was filtered into a half-liter flask, the residue and zinc hydroxide washed with hot water until free from iodine and the fluid made up to 500 cc. Fifty cc. of the solution were placed in a porcelain dish and titrated with silver nitrate, with potassium chromate as an indicator, until the end point, a slight brownish color, was reached.

The following results were obtained: Stas method—mean of five determinations gave 100.02 per cent.; second method—mean of five determinations gave 99.65 per cent. A sample of unpurified iodine gave, by this method, 98.83 per cent.

The iodine dried over the calcium chloride was tested for chlorine according to Fresenius,[1] but none was found.

For comparison, a sample of unpurified iodine was tested by the same method and the presence of the chlorine was indicated.

The following summary may be deduced from the foregoing research: (1) The Stas method gave the purest iodine; (2) sulphuric acid was the best drying agent; (3) the iodine was not contaminated when dried over calcium chloride; (4) the iodine, when pure, was satisfactorily determined when converted into zinc iodide and titrated with silver nitrate, with potassium chromate as an indicator.

A COLORIMETRIC METHOD FOR THE DETERMINATION OF SMALL QUANTITIES OF POTASSIUM.

By Lucian A. Hill.

Received July 11, 1903.

This method is primarily intended for use in the analysis of soil extracts and drainage waters where the potassium is in such small quantities that it is impracticable to use a gravimetric method. It has been used in this laboratory on a number of soil extracts, and has given very satisfactory results.

[1] "Qualitative Analysis."

The method depends upon the precipitation of the potassium in the usual way with chlorplatinic acid, and the subsequent reduction of the potassium chlorplatinate with stannous chloride in the presence of free hydrochloric acid. The precipitate of potassium chlorplatinate in very dilute solution is, of course, ver small, consisting of a few minute crystals. A distinct color is imparted to the solution on adding the stannous chloride solution, however, even though the original solution contained not more than one part of potassium oxide per million.

SOLUTIONS REQUIRED.

Standard Potassium Chlorplatinate.—0.518 gram of potassium chlorplatinate is dissolved in water and the solution made up to 100 cc. For use, 1 cc. of this solution is diluted to 100 cc. One cc. of the diluted solution is equivalent to 0.00001 gram potassium oxide.

Stannous Chloride.—Boil 75 grams of powdered or granulated tin with 400 cc. of concentrated hydrochloric acid in an Erlenmeyer flask until nearly all of the tin is dissolved. Keep in a tightly stoppered bottle over a small piece of tin.

Analytical Process.—The analytical process, up to the point of adding the stannous chloride, is essentially the same as that used in ordinary analysis.

To 50 cc. of the solution to be tested add 1 cc. of dilute sulphuric acid, evaporate to dryness, and ignite to whiteness. Dissolve the residue in hot water, acidified with a few drops of hydrochloric acid, and add an excess of chlorplatinic acid. The solution is then evaporated to a thick paste in a small dish and 80 per cent. alcohol added. Wash the precipitate thoroughly with 80 per cent. alcohol, then dissolve in boiling water, cool, and make up to a definite volume (100 or 200 cc.).

Transfer 50 cc. of this solution to a color-comparison cylinder and add 3 cc. of the stannous chloride solution. A yellow color is produced, the intensity of which is proportional to the amount of potassium chlorplatinate present. This color is exactly matched by introducing into other cylinders quantities of the standard potassium chlorplatinate solution and 3 cc. of the stannous chloride solution, as before. Below are given results obtained by this method:

Amount K_2O added. Parts per million.	Amount K_2O recovered. Parts per million.
1..... 1.0	0.92
2..... 1.0	0.8
3..... 1.0	1.0
4..... 1.0	1.2
5..... 2.0	1.9
6..... 2.0	2.1
7..... 2.0	2.0
8..... 2.0	2.0
9..... 3.0	3.2
10..... 3.0	3.2
11..... 3.0	2.8
12..... 3.0	2.8
13..... 4.0	4.4
14..... 4.0	4.0
15..... 4.0	4.0
16..... 4.0	4.4
17..... 5.0	5.0
18..... 5.0	5.0
19..... 5.0	4.9
20..... 10.0	11.6
21..... 10.0	11.2

NEW HAMPSHIRE COLLEGE,
AGRICULTURAL EXPERIMENT STATION.

THE DELICACY OF TESTS EMPLOYED FOR THE DETECTION OF METALS.

BY FLORENCE JACKSON.

Received June 24, 1903.

THE work in the following paper was undertaken for the purpose of determining the comparative delicacy of the tests employed in the ordinary methods used in qualitative analysis in detecting metals. To this end, solutions of salts were made of such strength that 1 cc. of the solution contained 5 mg. of the element under consideration or 1 part in 200. The weaker solutions were made from the standard by diluting with distilled water. When (as in the case of silver chloride) ammonia present in the water might exert a solvent influence, water free from ammonia was used. The reagents used were of the strength employed in the Wellesley College Chemical Laboratory (see table at the end), and were added drop by drop to 1 cc. of the solution under consideration.

The experiments were carried through twice, new standard solu-

tions being used the second time and, in cases of discrepancy, further tests were made.

The figures under the "final tests" were chosen as the probable limit of detection, if the element was not known to be present. They do not, therefore, usually represent the extreme limit indicated under the experimental conditions of this paper. This may account for the discrepancy between my figures and those given by other authorities.

FINAL TESTS. SUMMARY BY REAGENTS.

(*A*) HCl.

(*a*) Sp. gr. 1.035

Ag	1 : 64,000	1 : 1,000,000.	Comey.	Mulder.
		1 : 378,000.	Harting.	
		1 : 200,000.	Lassaigne.	
		1 : 189,000.	Pfaff.	
Hg^{I}	1 : 16,000	1 : 327,000.	Fresenius.	
Pb	1 : 500	1 : 1,077.	Wormley.	

(*b*) Sp. gr. 1.1 As above except

Hg^{I} 1 : 8,000

(*B*) NaCl.

Ag	1 : 32,000		
Hg^{I}	1 : 15,000		
Pb	1 : 1,000		

(*C*) H_2S.

As^{II}	1 : 1,024,000	1 : 13,200.	Wormley.	
Sb	1 : 512,000	1 : 24,000.	Wormley.	
Bi.Ag.Sn^{II}	1 : 64,000			
As.^{V} $Hg.^{I}$ Sn^{IV}	1 : 32,000	As 1 : 1530.	Wormley.	
Cd.Cu.Pb.Hg^{II}	1 : 16,000	Pb 1 : 1,000,000.	Prescott and Sullivan.	
		1 : 26,900.	Wormley.	
		Hg^{II} 1 : 46,000.	Green coloration	Lassaigne.
		1 : 23,000.	Brown "	
		1 : 6,770.	Wormley.	
		Cu 1 : 100,000.	Prescott and Sullivan.	
		1 : 12,500.	Wormley.	

(*D*) NH_4OH.

Mn	1 : 64,000			
Mg	1 : 32,000			
Co.Fe.^{III} Pb	1 : 16,000			
Al.Bi.Cu.Fe.^{II} $Hg.^{I-II}$ Sn.^{II} Zn	1 : 8,000	Hg^{II} 1 : 13,500.	Wormley.	
		Cu 1 : 20,000.	Prescott and Sullivan.	
		1 : 12,500.	Wormley.	
		Zn 1 : 12,500.	Wormley.	
Cd.Cr.Ni.Sn^{IV}	1 : 4,000			
Sb	1 : 1,000	1 : 1,200.	Wormley.	
Ag.(NH_4OH 1 : 10)	1 : 500			

(*E*) NaOH.

Mn	1 : 128,000			
Fe^{III}	1 : 32,000			
Al.Cu.Co.Hg^{I} Ni	1 : 16,000	Cu	1 : 125,000.	Wormley.
NH_3Bi.Cr.Fe^{II}Ag	1 : 8,000			
Cd.Zn	1 : 4,000			
Sn^{II-IV}	1 : 2,000			
Sb	1 : 1,000	1 : 1,200.	Wormley.	
Pb.Hg^{II}	1 : 500	Hg^{II}	1 : 677.	Wormley.

(*F*) K_2CrO_4.

Ba	1 : 256,000			
Pb	1 : 32,000	1 : 111,982.	Harting.	
		1 : 107,700.	Wormley.	
Cu	1 : 16,000	1 : 50,000.	Wormley.	
Ag	1 : 8,000			
Bi.Hg^{I}	1 : 4,000			
Cd	1 : 1,000			
Hg^{II}	1 : 333			
Sr	1 : 200			

(*G*) KI.

Ag.Cu.Pb.Hg^{I}	1 : 8,000	Ag	1 : 47,250.	Harting.
		Pb	1 : 21,540.	Wormley.
		Cu	1 : 12,500.	Wormley.
Hg^{II}	1 : 2,000	1 : 3,380.	Wormley.	

(*H*) Na_2HPO_4.

Mg	1 : 128,000	(Addition of NH_4Cl and NH_4OH.)
Ca	1 : 16,000	
Ag.Sr	1 : 8,000	
Ba	1 : 4,000	

(*I*) $(NH_4)_2S$.

Co	1 : 512,000	1 : 309,000.	Pfaff.
Fe^{II-III}	1 : 128,000		
Ni	1 : 64,000		
Al.Cr.Mn.Zn	1 : 8,000		

(*J*) H_2O.

Sb	1 : 2,000
Bi	1 : 4,000

(*K*) Na_2CO_3.

Sr	1 : 64,000			
Bi.Mn.Ag	1 : 32,000			
Cu.Fe^{III} Hg^{I} Ni	1 : 16,000	Cu	1 : 12,500.	Wormley.
Al.Ba.Co.Fe^{II}Zn	1 : 8,000	Zn	1 : 12,500.	Wormley.
Cd.Ca.Cr.Pb.Mg	1 : 4,000	Pb	1 : 53,850.	Wormley.
Hg^{II}	1 : 250			

(*L*) H_2SO_4.

Ba	1 : 256,000	1 : 79,300.	Harting.
Pb	1 : 16,000	1 : 21,540.	Wormley.
Sr	1 : 8,000	1 : 23,100-25,200.	Fresenius.
Ca	1 : 2,000		
Hg^{I}	1 : 1,000		

(*M*) $SnCl_2$.

Hg^{I}	1 : 32,000	
Hg^{II}	1 : 16,000	1 : 13,500. Wormley.

(*N*) KCN.

Co	1 : 16,000	
Cu.Ni	1 : 2,000	
Cd	1 : 1,000	

(*O*) $K_4Fe(CN)_6$.

Fe^{III}	1 : 64,000		
$Fe.^{II}Pb$	1 : 32,000	Pb	1 : 10,770. Wormley.
Cu	1 : 16,000		1 : 100,000. Prescott and Sullivan. 1 : 31,250. Wormley.

(*P*) $(NH_4)_2CO_3$.

Sr	1 : 16,000	1 : 95,200.	Comey.
Ca.Co.Fe^{III}	1 : 8,000	Ca 1 : 163,000.	Fresenius.
Ba.Fe^{II}	1 : 4,000	Ba 1 : 201,000.	Fresenius.
Mg	1 : 200		

(*Q*) $(NH_4)_2C_2O_4$.

Ca	1 : 64,000
Sr	1 : 32,000
Ba	1 : 2,000

(*R*) $CaSO_4$.

Ba	1 : 64,000
Sr	1 : 1,000

(*S*) H_2SiF_6.

Ba	1 : 2,000
K	1 : 200
Na	1 : 143

(*T*) H_2PtCl_6.

NH_3	1 : 2,000
K	1 : 200

STRENGTH OF REAGENTS EMPLOYED.

$(NH_4)_2CO_3$	175 grams to a liter + 100 cc. concentrated NH_4OH.
NH_4OH	Diluted 1 : 3 and 1 : 10.
$(NH_4)_2C_2O_4$	40 grams to a liter.
$(NH_4)_2S$	Saturate NH_4OH (0.96) with H_2S.
HCl	Sp. gr. 1.12 and 1.035.
HNO_3	Sp. gr. 1.2.
H_2SO_4	Diluted 1 : 5.
H_2S	From Kipp generator. Washed in H_2O.
$HgCl_2$	25 grams to a liter.
$MgSO_4$	50 " " " "
K_2CrO_4	50 " " " "
KCN	50 " " " "
KCNS	5 " " " "
$K_4Fe(Cn)_6$	75 " " " "
KI	25 " " " "
Na_2CO_3	250 " " " " Crystallized salt.
NaCl	50 " " " "
NaOH	150 " " " "
Na_2HPO_4	50 " " " "
$SnCl_2$	Sn dissolved in HCl + 4 parts of H_2O.

The results obtained from these experiments agree, in general, with facts already known. The work has value chiefly, as it seems to me, in the collection of definite data for future investigation rather than in any new facts brought to light by the figures given.

WELLESLEY COLLEGE,
June, 1903.

A LECTURE EXPERIMENT WITH AN UNDISSOCIATED SALT.

BY D. MCINTOSH.

Received June 18, 1903.

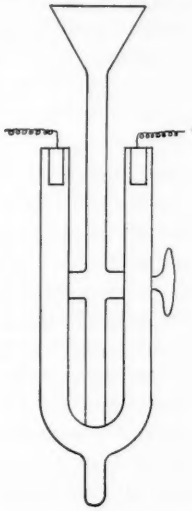
WHEN a sulphocyanate is added to a ferric salt, the deep red color produced is thought, for a number of reasons, to be due to the undissociated ferric sulphocyanate. These may be briefly stated: First, neither the ferric nor the sulphocyanate ion is colored; second, the crystals of ferric sulphocyanate, which can contain no ions, are similarly colored; third, in ether, in which salts are but slightly dissociated, the color is unchanged; fourth, an excess of a sulphocyanate increases the color, while the addition of sulphate ions weakens it.

If, then, ferric sulphocyanate were placed in a tube between two layers of a colorless liquid, the passage of a current should not increase the rate of diffusion; if, on the other hand, the color were due to a complex cation or anion, the color should move either to the cathode or anode.

If a solution of ferric sulphocyanate be placed in a U-tube, and carefully covered over with a less dense electrolyte (dilute hydrochloric acid), a current of $^1/_{100}$ ampere may be passed through it for several hours without the relative positions of the color-boundaries changing. The experiment can be made quite striking, by arranging in series two other tubes containing[1] potassium copper tartrate covered with dilute potassium hydroxide, and copper sulphate with ammonium hydroxide covered with ammonium hydroxide. In the first case, the color-boundaries remain stationary, while in the second and third they move towards the anode and cathode respectively.

[1] Massoni: *Ztschr. phys. Chem.*, **29**, 501 (1899).

In the figure is shown a U-tube of a convenient pattern, after Nernst. The lighter liquid is introduced first through the side tube. That the color is due to the undissociated salt is confirmed by conductivity and molecular-weight determinations. The conductivities of mixtures of ferric chloride and ammonium sulphocyanate were 20 to 30 per cent. less than their mean conductivities,



while the rise in boiling-point of a mixture of the two salts is always much less than the sum of the rise in boiling-points due to the two substances taken separately.

McGILL UNIVERSITY,
MONTREAL, April 25, 1903.

NOTES.

Note on Carbon Combustion in a Platinum Crucible.—In a recent paper[1] John V. R. Stehman, referring to the writer's special crucible[2] for carbon combustion, makes the statement that "the prevalent idea regarding his form of apparatus seems to be a fear of the rubber gasket causing error by burning directly or by be-

[1] This Journal, **25**, 237.
[2] *Ibid.*, **23**, 227, and **21**, 557.

coming hard and brittle, allowing small pieces to drop into the crucible when the stopper is pushed into place."

While it may be admitted that, prior to experience with the apparatus, such a fear is quite natural, the fact is that long use by many most careful chemists has proved this fear to be quite groundless. Even when the lower half of the crucible is hot enough to burn graphite in air, those parts of the apparatus which are in contact with the rubber gasket are so well cooled by the circulating water that the rubber is wholly unaffected. That there is no error from this cause is shown by the fact that the blanks are always under 0.0005 gram and that sharp results are easy to get on standard carbon samples.

However, a rubber band should not be used until it becomes hard and brittle, not so much from fear of rubber falling into the crucible as from the difficulty of getting a perfectly tight joint with the rubber in this condition.

While, therefore, there is no reason to fear the use of rubber, an asbestos gasket may be successfully used in place of it, if desired. For this purpose, cut a paper pattern, about one-half inch wide to fit accurately around the lower part of the stopper and overlapping about one-sixteenth of an inch at the ends. Cut asbestos paper, of the thickness of a rubber band, over this pattern. Soak the asbestos gasket at least twenty-four hours in a large beaker of water to extract all soluble carbonaceous matter; it is said dextrine is used as a binding material. Fit it, while wet, around the stopper, scraping it down carefully where the ends overlap. Saturate the gasket with water and press it, with a turning motion, into the crucible; there is no difficulty in getting a tight joint. Now test a succession of blanks, which, if the soluble carbonaceous matter has been well extracted, will not exceed 0.0005 gram. The asbestos must be well wetted before putting in the stopper and, just before beginning a combustion, it is well to place a few drops of water in excess around the upper part of the crucible. This will make any possible leak visible and will ensure a saturated and tight joint during the course of the combustion. The writer has tried an asbestos gasket with his crucible on carbon determination with results equally as satisfactory as with the rubber gasket. When determining combined water, however, rubber must be used, for wet asbestos is inadmissible and dry asbestos does not give a tight joint.

While on the subject of carbon determination, it may be well to call attention to two other matters of detail. The writer has recently seen copper oxide for combustion which, instead of having the usual dead-black color and porous appearance, had a reddish color and semi-fused appearance and was not as effective as an oxidizer.

The copper oxide for the small brass tube should be as fine as possible (free, of course, from powder), consistent with keeping the tube open and free. In filling the tube, unless special care is taken, the copper oxide particles may become wedged in spots, leaving empty spaces in the tube. The filling should be slow, using only a little copper oxide at a time and testing it constantly with a wire to be sure the tube is full in every part where it is to be heated.

Where water-bottles are used for furnishing the air-pressure it is well to use water in which a little cupric sulphate has been dissolved. The solution is filtered and, being an inhospitable field for bacterial activity, remains clear and free from the carbonaceous gases which are given off from stagnant water in sufficient amount to affect carbon determinations.

PORTER W. SHIMER.

LABORATORY OF P. W. SHIMER, EASTON, PA.

The Color Test in High Carbon Steels.—Parker says of it that it is "liable to great variations";[1] Galbraith that it "should be abandoned";[2] Tucker, that "its inaccuracy is well recognized";[3] Hadfield that "it had long been a matter of knowledge in the Sheffield steel trade, that the color test was apt to give misleading results";[4] Metcalf in his book "Steel" characterizes it as "the wildest guess work in the best hands." Campbell in his book "The Manufacture and Properties of Iron and Steel," and elsewhere, repeatedly and emphatically expresses distrust of the method.

It is the writer's experience also that the color method as usually carried out is unreliable. The same drillings do not always dissolve to the same shade. This difficulty can only be overcome by the use of two precautions not generally known and practiced. (1) One gram must be taken.[5] (2) The acid must, before using,

[1] *Chem. News*, **42**, 88.
[2] *Journal Iron and Steel Institute*, **181**, 234.
[3] *Ibid.*, **96**, 1, 137.
[4] *Ibid.*, **96**, 2, 187.
[5] Weighed out into a 41 cc. test-tube provided with a mark at 25 cc. Twenty cc. acid is used for solution. After cooling, the liquid is diluted to the mark, mixed by placing the thumb over the tube and inverting a number of times, and 5cc. withdrawn for comparison.

be made ice-cold by immersing a beaker of it in a larger beaker of ice and water for some time; it must be added all at once, and, instead of simply having the test-tube stand in cold water, it must be moved rapidly and vigorously around in a large beaker of ice-water for a minute after the addition of the acid, and before standing in the water-bath filled with cold (not necessarily ice-cold) water.[1] Dissolving in this way, no violent action takes place; loss of hydrocarbon gas is avoided—or if there is loss, it is a uniform one; and reasonable accuracy for practical purposes is insured. Results, however, are still not so reliably accurate as by combustion, for the reason that even in the same kind of steels the proportion of hardening carbon (which gives no color in the color test) to carbide carbon is not always the same. Fifty consecutive heats of high-carbon open-hearth steel, tested in the manner above described, and also by combustion, showed forty-eight fairly good results by the color method (mostly within 0.03 per cent. of the truth—a few to 0.04 per cent.), and two results (duplicated by both methods) 0.06 per cent. wide of the truth. The standard should be made up of drillings from many different heats mixed together, as was the case here. Crucible steel would show less variation in proportion of hardening to carbide carbon.

GEORGE AUCHY.

NEW BOOKS.

DES INDUSTRIES CHIMIQUES ET PHARMACEUTIQUES. PAR ALBIN HALLER, Membre de l'Institut, Professeur à la Faculté des Sciences de Paris, Rapporteur du Jury de la Classe 87 à l'Exposition Universelle de 1900. Paris: Gauthier-Villars, 1903. 2 vols. quarto. Vol. I, lxxxix + 405 pp. Vol. II, 544 pp. Price, 20 francs.

Perhaps nothing more strikingly illustrates the enormous development of technical chemistry in the last generation than does a comparison of this work of Haller with the famous *Bericht* of A. W. Hofmann, published after the Vienna exposition of 1873. The work of Hofmann was a masterpiece in its way and is still the authority which must be studied in any discussion of the development of chemical manufactures. The number of exhibitors of chemical products at Vienna was not great, but, in discussing the things there shown, opportunity was taken to give a pretty full

[1] If the violent action be prevented at the very start it does not occur at all.

survey of the state of all important chemical industries at the time. Hofmann's *Bericht* is made up really of a series of short monographs by competent authorities.

The work of Haller is also a masterpiece, although in detail it is very different from the book of the Berlin professor. While information is drawn from many sources, the composition appears to be the work of the industrious author alone. At the outset, one is impressed with the great increase of exhibitors in 1900 over 1873, and with the enormous expansion of the industries described.

The Haller report opens with a lengthy general introduction in which is discussed, and very fairly too, the condition of chemical industry in the several countries represented at the exposition. Recognizing the peculiar advanced position occupied by Germany in this field, the author addresses himself to the solution of the question which has attracted so much attention in France, and especiallly in England in the last ten or fifteen years: Why is the German chemical industry so much in advance of that of other nations? Like the English writers before him, Haller reaches the conclusion that the extraordinary development of the German higher education in the universities and technical schools is the most potent factor in explaining German ascendancy in chemical manufacture. Interesting figures are quoted showing the large sums which have been spent in developing certain of the German laboratories, and on the subject of salaries also something is said which appears surprising to the American reader, who has been so often told that the German professors are very poorly paid for their services.

With respect to the higher chemical education in the United States the remarks of Haller are appreciative and sympathetic. He quotes, at length, from a letter to the *Chemiker Zeitung*, written by Dr. Schneider, at one time professor at the University of Chicago, in which some of our institutions are described in rather dark colors, but explains further that Schneider's picture is somewhat overdrawn. Haller spent some months in this country at the time of the Chicago exposition and wrote a valuable report to his government on his return in which he discussed educational as well as technical matters. He visited several of our larger schools while here, and his observations are of value. "That more is not accomplished with the colossal resources at the disposition of the universities, is the other side of the problem, but each

country must have its own standards, and work things out in its own time." Part of the trouble here, the author very truly says, is found in the condition of our secondary education.

In this introduction, finally, fourteen pages are devoted to the topic "Instruction in Chemistry in France." This will be found instructive reading, since the author has had himself much to do with the awakening now discernible in his country. Throughout there is a comparison with German conditions and methods which cannot fail to incite his countrymen to greater efforts.

The body of the work is made up of ten chapters dealing with different lines of chemical industry. The first and longest of these is devoted to the so-called heavy chemicals, the common acids, alkalies, bleaching-powder, phosphates, nitrates, Stassfurt salts, etc., while the following chapters deal with special fields of work—colors, varnishes, soaps, medicinal chemicals, crude colonial products and so on. Everything from artificial silk to the ozone purification of water seems to be considered, and the discussion is not confined to things exhibited at Paris, but is made complete with much matter drawn from other sources. The author discusses very satisfactorily the great advances which have been made in most of the important chemical industries in the ten years following the earlier French exposition of 1889, and gives for reference numerous bibliographical tables, by the aid of which further information may be obtained. Unusually full statistical information is given regarding such great enterprises as the "Badische Anilin und Soda Fabrik," the "Farbenfabriken vorm. Friedrich Bayer und Co.," the "Farbwerke vorm. Meister, Lucius und Brüning," and others.

Apparently but few chemical exhibits were sent from the United States and some of these were not to our credit or in any way a proper measure of our industry. Haller calls attention to the last and explains that in many directions chemical manufacturers have made colossal advances in this country, that indeed in some important lines we are becoming exporters instead of importers. The development of the electrochemical industries is especially mentioned.

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